30697

NATIONAL LIBRARY
OTTAWA

CANADA

BIBLIOTHÈQUE NATIONALE
OTTAWA

NAME OF AUTHOR.....W. H. HARGROVE.....

TITLE OF THESIS...CONCENTRATION..FLUCTUATIONS...AND..
STRUCTURE..FACTORS..of..BINARY.....
..LIQUID....MIXTURES.....

UNIVERSITY...of....ALBERTA.....

DEGREE FOR WHICH THESIS WAS PRESENTED.....Ph.D.....

YEAR THIS DEGREE GRANTED.....1976.....

Permission is hereby granted to THE NATIONAL LIBRARY OF CANADA to microfilm this thesis and to lend or sell copies of the film.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

(Signed).W. Hall. Hargrove.

PERMANENT ADDRESS:

....8008-115 STREET....
....EDMONTON, ALBERTA
.....

DATED...MAY 18.....1976

NL-91 (10-68)

INFORMATION TO USERS

THIS DISSERTATION HAS BEEN
MICROFILMED EXACTLY AS RECEIVED

This copy was produced from a microfiche copy of the original document. The quality of the copy is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Canadian Theses Division
Cataloguing Branch
National Library of Canada
Ottawa, Canada K1A ON4

AVIS AUX USAGERS

LA THESE A ETE MICROFILMEE
TELLE QUE NOUS L'AVONS RECUE

Cette copie a été faite à partir d'une microfiche du document original. La qualité de la copie dépend grandement de la qualité de la thèse soumise pour le microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

NOTA BENE: La qualité d'impression de certaines pages peut laisser à désirer. Microfilmee telle que nous l'avons reçue.

Division des thèses canadiennes
Direction du catalogage
Bibliothèque nationale du Canada
Ottawa, Canada K1A ON4

THE UNIVERSITY OF ALBERTA

CONCENTRATION FLUCTUATIONS AND STRUCTURE FACTORS OF BINARY LIQUID MIXTURES

by

WILLIAM HALDEN HARGROVE (C)

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

IN

PHYSICS

DEPARTMENT OF PHYSICS

EDMONTON, ALBERTA

FALL , 1976

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled CONCENTRATION FLUCTUATIONS AND STRUCTURE FACTORS OF BINARY LIQUID MIXTURES submitted by William Halden Hargrove in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics.

.....
Supervisor

.....

.....

.....

.....
External Examiner

DATED: May 10, 1976

ABSTRACT

This thesis is concerned with an investigation of the behaviour of the various structure factors, especially of their long wavelength (wave number $q \to 0$) limits, for different types of mixtures.

First we examine the behaviour of the $q \to 0$ limits of the concentration fluctuations $S_{CC}(q \to 0)$ and the various partial structure factors $a_{ij}(0)$, using the model of conformal solutions. The model is applicable to systems in which (a) the two types of atoms (A and B) are of roughly the same size, and (b) the difference ω in pairwise interaction energies between the atoms is small (for an ideal solution $\omega = 0$). It is found that the interchange energy ω is directly related to $S_{CC}(0)$ or the combination $a_{11}(0) + a_{22}(0) - 2a_{12}(0)$. The model is applied to calculate $a_{ij}(0)$ for Na-K alloys and good agreement with experiment is found. The behaviour of $S_{CC}(0)$ for alloys where the assumption (a) above does not hold is also discussed, using Flory's approximation.

Next, a phenomenological model is proposed to calculate $S_{CC}(0)$ and other thermodynamic properties of systems in which the interatomic interactions are strong and which form compounds in the solid phase at one or more well defined stoichiometric compositions specified by $A_\mu B_\nu$ (μ, ν small integers). It is assumed that the

binary liquid mixture consists of A and B atoms and their chemical associations $A_\mu B_\nu$ in chemical equilibrium. The formulation is given in general terms, but the actual calculations are made by assuming that only one type of chemical associations is formed. By assuming first, for simplicity, that the mixture of A, B and $A_\mu B_\nu$ can be considered ideal, it is shown that the concentration dependence of $S_{CC}(0)$ and hence of the various $a_{ij}(0)$ depend characteristically on the values of (μ,ν). The results for $S_{CC}(0)$ for $(\mu,\nu) = (3,2)$, $(3,1)$ and $(2,1)$ are in qualitative agreement with those determined from measured thermodynamic activity data for Mg-Bi, Ag-Al and Hg-K. It is then shown by numerical calculations for four systems (Mg-Bi, Tl-Te, Ag-Al and Cu-Sn) that quantitative agreement with experiment can be achieved if the ternary mixture of A, B and $A_\mu B_\nu$ is treated in either the conformal or Flory's approximations, the interaction parameters being determined from the observed free energy. It is concluded that evidence for the formation of chemical complexes should be sought by making neutron scattering experiments.

Finally, a simple modification (based on the random phase approximation) of the usual hard sphere calculations of the structure factors, at arbitrary q, is proposed to take into account the effect of the long range attractive interactions in weakly interacting

systems. The method is first applied to calculate S(q) for liquid argon obtaining good agreement with experiment. Next, some numerical examples are given for mixtures. One finds that the effect of the attractive interactions may be expected to be limited to q values in the range $0 < q < q_o$, where q_o is the position of the main peak in $a_{ij}(q)$. The significance of these results to the calculation of electrical resistivity, etc. is briefly discussed.

ACKNOWLEDGMENT

It is unfortunate that limitations of space and decorum preclude adequate acknowledgment of the contributions of my supervisor, Dr. A.B. Bhatia, to this work. I can only express my sincere gratitude for his liberal guidance and for his abundant inspiration, patience and understanding which, regrettably, my shortcomings necessitated in full measure.

My thanks are also due to Professor N.H. March for generous help and encouragement on several occasions.

Over parts of the considerable period of time these studies have spanned, the National Research Council and the University of Alberta have been financially supportive while the acquaintance of numerous staff members and fellow students has been mentally sustaining.

TABLE OF CONTENTS

		Page
CHAPTER 1	INTRODUCTION	1
CHAPTER 2	STRUCTURE FACTORS AND THEIR LONG WAVELENGTH LIMITS	6
2.1	Definitions of the Structure Factors	6
2.2	Sum Rules and Constraints	11
2.3	Long Wavelength Limits of the Structure Factors	14
CHAPTER 3	CONCENTRATION FLUCTUATIONS AND PARTIAL STRUCTURE FACTORS IN IDEAL AND WEAKLY INTERACTING MIXTURES	20
3.1	Introduction	20
3.2	Ideal Solution	22
3.2.1	G_M, κ_T, δ and S_{CC}	22
3.2.2	Partial Structure Factors	23
3.3	Partial Structure Factors in Low Concentration Limit	25
3.4	Regular Solutions in the Zeroth Approximation	30
3.4.1	Expression for the Free Energy	30
3.4.2	Expressions for V, δ, κ_T and S_{CC}	35
3.4.3	Expressions for the Partial Structure Factors	37
3.5	Application of Regular Solution Theory to Na-K	39
3.5.1	Comparison with Experiment for S_{CC}, V and κ_T	39

		Page
CHAPTER 3	(cont'd)	
	3.5.2 Partial Structure Factors	41
	3.5.3 Concluding Remarks	47
3.6	Effect of Size Difference on Concentration Fluctuations in Weakly Interacting Systems	48
CHAPTER 4	CONCENTRATION FLUCTUATIONS IN PARTIAL STRUCTURE FACTORS OF COMPOUND FORMING BINARY MOLTEN ALLOYS	51
4.1	Introduction and Model	51
4.2	Expressions for G and S_{CC}	54
4.3	Expressions for S_{CC} etc. for Single Pair of (μ,ν) and the Ideal Solution Assumption	59
4.4	Concentration Fluctuations S_{CC} for Different μ,ν	62
	4.4.1 Limiting Cases	62
	4.4.2 Discussion and Numerical Results	66
4.5	Variation of Partial Structure Factor with Concentration	76
CHAPTER 5	CONCENTRATION FLUCTUATIONS AND THERMODYNAMIC PROPERTIES OF SOME COMPOUND FORMING BINARY MOLTEN SYSTEMS	84
5.1	Introduction	84
5.2	Basic Formulae and Approximations	86
5.3	Expressions for Various Thermodynamic Quantities	91
	5.3.1 Approximation (a)	91
	5.3.2 Approximation (b)	95
5.4	Expressions for S_{CC} for Two Limiting Case	97

		Page
CHAPTER 5	(cont'd)	
5.5	Numerical Results	103
5.6	Discussion and Concluding Remarks	122
CHAPTER 6	THE STRUCTURE FACTORS FOR ARBITRARY q INTERACTING BINARY MIXTURES	126
6.1	Introduction	126
6.2	Basic Equations	128
6.2.1	Direct Correlation Functions and Structure Factors	128
6.2.2	P-Y Approximation and Hard Sphere Model	132
6.3	A Modification of the Hard Sphere Model	134
6.4	Numerical Calculations	138
6.4.1	Calculations for Liquid Argon	138
6.4.2	Mixture	140
6.5	Discussion and Concluding Remarks	152
BIBLIOGRAPHY		157
APPENDIX 1		161

LIST OF TABLES

Table		Page
4.1	The positions ($\tilde{c}_1$ and $\tilde{c}_2$) and heights of the peaks in S_{CC} for the limiting case $K \to 0$ for some pairs of μ,ν.	69
5.1	Interaction parameters for the systems Tl-Te, Mg-Bi, Ag-Al and Cu-Sn in the approximations (a) and (b).	106

LIST OF FIGURES

Figure		Page
3.1	Variation of dilatation factor δ with concentration for a mixture obeying Vegard's law.	24
3.2	Variation of a_{ij} with concentration in an ideal solution taking $\theta = 0$ and $\beta = V_1^{(o)}/V_2^{(o)} = 2$.	26
3.3	Variation of a_{ij} with concentration in an ideal solution taking $\theta = 0$ and $\beta = 1/2$.	27
3.4	Variation of S_{CC} with concentration for regular solutions in the zeroth approximation.	36
3.5	Variation of $a_{11}+_{22}-2a_{12}$ with concentration according eq. (3.40).	40
3.6	Molar volume against potassium concentration for Na-K alloys at 100°C.	42
3.7	Volume times compressibility against potassium concentration for Na-K alloys at 100°C.	43
3.8	Dilatation factor δ versus sodium concentration for Na-K alloys for several values of α'.	44
3.9	Variation of a_{ij} with concentration for Na-K alloys at 100°C.	46
3.10	Variation of S_{CC} with concentration in Flory's approximation (eq. (3.44)) for volume ratio $\beta = 1/3$ and several values of ω/RT.	50

Figure		Page
4.1	The concentration fluctuations S_{CC} as a function of concentration in a binary mixture forming chemical associations of the AB type ($\mu=\nu=1$).	70
4.2	S_{CC} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the A_3B_2 type ($\mu=3$, $\nu=2$).	71
4.3	S_{CC} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the A_3B_1 type ($\mu=3$, $\nu=1$).	72
4.4	S_{CC} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the $A_\mu B_\nu$ type ($\mu=2$, $\nu=1$).	73
4.5	The partial structure factors a_{ij} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the $A_\mu B_\nu$ type.	79
4.6	The partial structure factors a_{ij} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the type A_3B_2 ($\mu=3$, $\nu=2$).	80
4.7	The partial structure factors a_{ij} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the type A_2B_1 ($\mu=2$, $\nu=1$).	81
5.1a	$G_M/\mathcal{N}RT$ and $n_3/\mathcal{N}$ as functions of concentration for Tl-Te.	107
5.1b	$G_M/\mathcal{N}RT$ and $n_3/\mathcal{N}$ as functions of concentration for Mg-Bi.	108
5.1c	$G_M/\mathcal{N}RT$ and $n_3/\mathcal{N}$ as functions of concentration for Ag-Al.	109
5.1d	$G_M/\mathcal{N}RT$ and $n_3/\mathcal{N}$ as functions of concentration for Cu-Sn.	110

Figure		Page
5.2a	The logarithm of the activity, ln a_{Tl}, versus concentration for Tl-Te.	111
5.2b	The logarithm of the activity, ln a_{Mg}, versus concentration for Mg-Bi.	112
5.2c	The logarithm of the activity, ln a_{Ag}, versus concentration for Ag-Al.	113
5.2d	The logarithm of the activity, ln a_{Cu}, versus concentration for Cu-Sn.	114
5.3a	The concentration fluctuation S_{CC} versus concentration for Tl-Te.	115
5.3b	The concentration fluctuation S_{CC} versus concentration for Mg-Bi.	116
5.3c	The concentration fluctuation S_{CC} versus concentration for Ag-Al.	117
5.3d	The concentration fluctuation S_{CC} versus concentration for Cu-Sn.	118
5.4	Heat and entropy of mixing for Tl-Te system.	121
6.1	Sketch of the model potential showing $\phi(r)$ of Lennard-Jones form and $\chi(r)$ as well as the hard core.	139
6.2	Model S(q) for $\varepsilon/k_B = 123°K$, $r_o = 3.4\times10^{-8}$ cm and $\sigma = 0.98\ r_o$ compared with experimental S(q) for Ar at 85°K.	141
6.3a	Model $\theta(q)$, $S_{CC}(q)$ and $\Delta(q)$ for two concentrations (c = 1/2, c = 1/5) taking R = 0.10, T = 85° (i.e. critical parameters).	146
6.3b	Model $a_{ij}(q)$ for the same parameters as Fig. 6.3a.	147
6.4a	Model $\theta(q)$, $S_{CC}(q)$ and $\Delta(q)$ at an elevated temperature: $T = 3/2\ T_c$ with R = 0.1 ($T_c = 85°K$).	148
6.4b	Model $a_{ij}(q)$ for the same parameters as Fig. 6.4a.	149

Figure		Page
6.5a	Model $\theta(q)$, $S_{CC}(q)$ and $\Delta(q)$ for $R = -0.2$, $T = 85°K$ for two concentrations.	150
6.5b	Model $a_{ij}(q)$ for the same parameters as Fig. 6.5a.	151
6.6	$S_{CC}(q)$ for two values of R at $T = 85°K$.	153

CHAPTER 1

INTRODUCTION

This thesis is concerned with a study of, firstly, the long wavelength (wavenumber $q \to 0$) limits of the structure factors of binary molten alloys whose constituent atoms interact with one another either weakly or strong, and, secondly, the structure factors at all q for weakly interacting systems.

The structure factors play an important role in our understanding of interatomic interactions, on the one hand, and of various transport properties of molten alloys, on the other; for an exhaustive review, see Faber (1972).

The structure of (relative arrangement of atoms in) a pure liquid is described by a single structure factor S(q) which is essentially the Fourier transform of the pair distribution function g(r) [see Chapter 2]. Since X-ray or neutron scattered intensities are directly proportional to S(q), its experimental determination is a straightforward matter. On the theoretical side, there have been many attempts to calculate S(q); notable are those using the hard sphere model in the Percus-Yevick approximation [Ashcroft and Lekner (1966), etc.] and modifications thereof [Woodhead-Galloway and Gaskell (1968), etc.].

For a comprehensive list of references see, for example, Croxton (1974). In the zero-wavenumber limit, however, S(0) can be exactly expressed in terms of certain thermodynamic quantities via the Einstein-Smoluchowski or Ornstein-Zernike relation:

$$S(0) = \frac{N}{V} k_B T \kappa_T \qquad (1.1)$$

where κ_T is the isothermal compressibility, N is the total number of atoms in volume V, T is the temperature, and k_B is the Boltzmann constant.

In a binary A-B mixture there are three independent structure factors corresponding, basically, to the correlations between A-A atom pairs, B-B atom pairs and A-B atom pairs. There are several equivalent (linearly related) sets of structure factors defined in the literature: for example, the partial structure factors $a_{ij}(q)$, or $S_{ij}(q)$ [Faber and Ziman (1965), Ashcroft and Langreth (1967)], and the number-concentration-structure factors $S_{NN}(q)$, $S_{NC}(q)$ and $S_{CC}(q)$ [Bhatia and Thornton (1970, 1971)].

The expression for the scattered intensity for X-rays or neutrons now involves, in general, all three structure factors (all $a_{ij}(q)$, or $S_{ij}(q)$, etc.), and experimental determination of them involves varying the coefficients in the expression for scattering. Where practical, this can be done for

neutron scattering by using different isotopes of one of the components in the mixture. The actual determination of the structure factors has been achieved only for a few cases [Enderby, North and Egelstaff (1966), Page and Mika (1971)]. The theoretical calculations of $S_{ij}(q)$ for a binary mixture are mainly those using the hard sphere model in the Percus-Yevick approximation [Lebowitz (1964), Ashcroft and Langreth (1967), Enderby and North (1968)].

The long wavelength ($q \to 0$) limits of the structure factors are naturally hard to determine from scattering experiments, and one must turn to other considerations to obtain information on them. Recently Bhatia and Thornton (1970) have shown that the $q \to 0$ limits of the structure factors may be determined from a knowledge of three thermodynamic quantities: the compressibility, the volume as a function of composition and $S_{CC}(0)$ (the mean square fluctuation in concentration). The latter quantity ($S_{CC}(0)$) depends on the second derivative of the free energy of mixing with respect to the concentration and, as we shall see later, reflects rather sensitively the nature of the interatomic interactions in the mixture.

In Chapter 3 of the thesis, we investigate the behaviour of $S_{CC}(0)$ and other structure factors

(in $q \to 0$ limit), using the well known theoretical model of regular solutions (in the zeroth approximation). This model is applicable to systems in which (a) the two types of atoms are of roughly the same size, and (b) the differences in pairwise interactions between the atoms is small. These conditions are approximately fulfilled in many systems, e.g. Na-K. Detailed calculations are given for the Na-K system and are found to be in good agreement with experiment [McAlister and Turner (1972)]. This chapter also discusses qualitatively the behaviour of $S_{CC}(0)$ when the two types of atoms have significantly different size.

There are, however, a number of systems (e.g. K-Hg, Mg-Bi, Ag-Al, Tl-Te, etc.) where the differences in the interactions between the two species is not small. This is evidenced by the fact, amongst others (magnitude of molar free energy of mixing relative to RT, etc.), that in the solid phase they form intermetallic compounds at one or more well-defined chemical compositions. The main body of the thesis (Chapters 4 and 5) is devoted to a discussion of the concentration dependence of $S_{CC}(0)$ and other thermodynamic properties of such compound-forming systems.

In Chapter 4 we first describe a theoretical model to obtain an expression for the free energy G of the compound-forming molten systems. The model

essentially consists of assuming the existence of appropriate chemical complexes $A_\mu B_\nu$ in chemical equilibrium with one another; here μ, ν are small non-zero integers. Although a general formulation is given, the actual calculations can be made only under certain simplifying approximations. In the remainder of the chapter we examine, in a simple approximation, the general features of $S_{CC}(0)$ and of partial structure factors for different values of μ and ν.

Next (Chapter 5), we discuss two higher approximations to the free energy and calculate therefrom $S_{CC}(0)$ and other thermodynamic quantities. It is shown by taking several examples that the model gives quantitative agreement with experiment.

Finally, in Chapter 6, an approximate model is used to discuss some qualitative features of the structure factors of weakly interacting systems, away from the long wavelength limit (i.e. $q > 0$).

CHAPTER 2

STRUCTURE FACTORS AND THEIR LONG WAVELENGTH LIMITS

As mentioned earlier, there are several equivalent sets of structure factors for binary mixtures used in the literature. In this chapter we define three sets and give, for them, certain results which will be found useful in later chapters.

2.1 Definitions of the Structure Factors

The most commonly used set of structure factors are perhaps the partial interference functions $a_{\alpha\beta}(q)$ of Faber and Ziman (1965) defined by ($\alpha,\beta = 1,2$)

$$a_{\alpha\beta}(q) = 1 + \frac{N}{V}\int e^{i\vec{q}\cdot\vec{r}}(g_{\alpha\beta}(r) - 1)d^3r \qquad (2.1)$$

where $g_{\alpha\beta}(r) = g_{\beta\alpha}(r)$ is the pair distribution function defined as the probability, normalized to unity for large r, of finding an atom of type β in a unit volume at a radius r from the centre of a type α atom. Because of the spherical symmetry of $g_{\alpha\beta}(r)$ in an isotropic liquid, the $a_{\alpha\beta}(q)$ depends, of course, only on the magnitude of $\vec{q}$ (and not on its direction).

Another set of structure factors $S_{\alpha\beta}(q)$ which are frequently used, are defined as [Ashcroft and Langreth (1967), Enderby and North (1968)]

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + (c_\alpha c_\beta)^{\frac{1}{2}} \frac{N}{V} \int e^{i\vec{q}\cdot\vec{r}} [g_{\alpha\beta}(r) - 1] d^3r \quad (2.2)$$

where c_α is the concentration of α-type atoms in the mixture. If N_1 and N_2 denote the numbers of the two types of atoms respectively, $N = N_1 + N_2$ and†

$$c_1 = \frac{N_1}{N} \qquad c_2 = \frac{N_2}{N} \quad , \quad c_1 + c_2 = 1. \quad (2.3)$$

Comparing with (2.1) and (2.2) one has

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + (c_\alpha c_\beta)^{\frac{1}{2}} [a_{\alpha\beta}(q) - 1] \quad . \quad (2.4)$$

Finally, a set which we find particularly useful are the number-concentration structure factors $S_{NN}(q)$, $S_{CC}(q)$ and $S_{NC}(q)$ [Bhatia and Thornton (1970)]. These are defined in the following manner.

Let $n_\alpha(\vec{r})$ ($\alpha = 1,2$) denote the local number density of α-type atoms and let their mean density be denoted by $\bar{n}_\alpha (= N_\alpha/V)$. Then the deviation $\delta n_\alpha(\vec{r})$ from the mean is:

$$\delta n_\alpha(\vec{r}) = n_\alpha(\vec{r}) - \bar{n}_\alpha = -\bar{n}_\alpha + \sum_{j=1}^{N_\alpha} \delta(\vec{r} - \vec{R}_j^\alpha) \quad , \quad (2.5)$$

where $\vec{R}_j^\alpha$ is the position of the j^{th} atom of type α. Making the Fourier expansion

---

† In the following, it will sometimes be convenient to write the concentrations c_1 and c_2 also as

$$c_1 \equiv c \quad , \quad c_2 = 1 - c_1 = 1 - c \quad .$$

$$\delta n_\alpha(\vec{r}) = \frac{1}{V} \sum_q N_\alpha(\vec{q}) e^{-i\vec{q}\cdot\vec{r}} \quad , \tag{2.6}$$

$$N_\alpha(\vec{q}) = \int e^{i\vec{q}\cdot\vec{r}} \delta n_\alpha(\vec{r}) d^3r$$

$$= \sum_{j=1}^{N_\alpha} e^{i\vec{q}\cdot\vec{R}_j^\alpha} - N_\alpha \delta_{q,o} \quad . \tag{2.7}$$

The reality of $\delta n_\alpha(r)$ requires that $N_\alpha^*(q) = N_\alpha(-q)$. Similarly, if $N(\vec{q})$ denotes the Fourier transform of the local deviation $\delta n(\vec{r})$ in the total number density $n(\vec{r}) = n_1(\vec{r}) + n_2(\vec{r})$, then

$$N(\vec{q}) = \sum_{\alpha=1,2} e^{i\vec{q}\cdot\vec{R}_j^\alpha} - N\delta_{q,o}$$

$$= N_1(\vec{q}) + N_2(\vec{q}) \quad . \tag{2.8}$$

We next define the local deviation from the mean concentration $c(\equiv c_1)$ by

$$\delta c(\vec{r}) = \frac{V}{N} [(1-c)\delta n_1(\vec{r}) - c\delta n_2(\vec{r})] \quad , \tag{2.9}$$

so that if δn_1 and δn_2 change in proportion to their respective mean concentrations, namely, c and (1-c), then $\delta c(\vec{r}) = 0$, as it should. If we make the Fourier expansion

$$\delta c(\vec{r}) = \sum_q C(\vec{q}) e^{-i\vec{q}\cdot\vec{r}} \tag{2.10}$$

then

$$C(q) = \frac{1}{V}\int \delta c(\vec{r})\, e^{i\vec{q}\cdot\vec{r}}$$

$$= \frac{1}{N}\left[(1-c)N_1(\vec{q}) - cN_2(\vec{q})\right] . \qquad (2.11)$$

The number-concentration structure factors are now defined by

$$S_{NN}(\vec{q}) = \frac{1}{N}\langle N^*(\vec{q})N(\vec{q})\rangle \qquad (2.12a)$$

$$S_{CC}(\vec{q}) = N\langle C^*(\vec{q})C(\vec{q})\rangle \qquad (2.12b)$$

$$S_{NC}(\vec{q}) = \frac{1}{2}\langle N^*(\vec{q})C(\vec{q}) + N(\vec{q})C^*(\vec{q})\rangle \qquad (2.12c)$$

where $\langle\ldots\rangle$ represents thermal (ensemble) average. Like $a_{\alpha\beta}(q)$ and $S_{\alpha\beta}(q)$, $S_{NN}(q)$ etc. for an isotropic liquid are also independent of the direction of $\vec{q}$.

To see how these different sets of structure factors are related to one another, one has only to note that the pair distribution function $g_{\alpha\beta}(r)$ is, by definition,

$$g_{\alpha\beta}(r) = \frac{1}{V}\int d^3r_o \, \frac{\langle n_\alpha(\vec{r}_o)\left[n_\beta(\vec{r}_o+\vec{r}) - \delta_{\alpha\beta}\delta(\vec{r})\right]\rangle}{\langle n_\alpha(\vec{r}_o)\rangle\langle n_\beta(\vec{r}_o+\vec{r})\rangle} . \qquad (2.13)$$

Using for $n_\alpha(\vec{r})$, etc. the expansion (2.5) and noting that $\langle n_\alpha(r)\rangle = \bar{n}_\alpha$, it may be seen that $S_{\alpha\beta}(q)$ may also be written as

$$S_{\alpha\beta}(q) = \frac{1}{2N(c_\alpha c_\beta)^{\frac{1}{2}}}\langle N_\alpha^*(\vec{q})N_\beta(\vec{q}) + N_\alpha(\vec{q})N_\beta^*(\vec{q})\rangle . \qquad (2.14)$$

Since from (2.8) and (2.11)

$$N_1(\vec{q}) = cN(\vec{q}) + NC(\vec{q}) , \quad N_2(\vec{q}) = (1-c)N(\vec{q}) - NC(\vec{q}) \tag{2.15}$$

one can immediately write down the $S_{\alpha\beta}(q)$ in terms of $S_{NN}(q)$ etc., and hence using (2.4) also the $a_{\alpha\beta}(q)$ in terms of $S_{NN}(q)$ etc. We give here explicitly the relations between $a_{\alpha\beta}(q)$ and $S_{NN}(q)$ etc. [Bhatia and Thornton (1970)]

$$c_1^2 a_{11}(q) = c_1^2 S_{NN}(q) + 2c_1 S_{NC}(q) + S_{CC}(q) - c_1 c_2 \tag{2.16a}$$

$$c_2^2 a_{22}(q) = c_2^2 S_{NN}(q) - 2c_2 S_{NC}(q) + S_{CC}(q) - c_1 c_2 \tag{2.16b}$$

$$c_1 c_2 a_{12}(q) = c_1 c_2 S_{NN}(q) + (c_2 - c_1) S_{NC}(q) - S_{CC}(q) + c_1 c_2 \tag{2.16c}$$

and conversely

$$S_{NN}(q) = c_1^2 a_{11}(q) + c_2^2 a_{22}(q) + 2c_1 c_2 a_{12}(q) \tag{2.17a}$$

$$S_{NC}(q) = c_1 c_2 [c_1 (a_{11}(q) - a_{12}(q)) - c_2 (a_{22}(q) - a_{12}(q))] \tag{2.17b}$$

$$S_{CC}(q) = c_1 c_2 [1 + c_1 c_2 (a_{11}(q) + a_{22}(q) - 2a_{12}(q))] . \tag{2.17c}$$

2.2 Sum Rules and Constraints

It is next of interest to give the sum rules satisfied by the various structure factors defined above.

First consider the sum rules for the number-concentration structure factors [Bhatia and Thornton (1970)]. For $S_{NN}(q)$, we have from (2.12a) and (2.8)

$$S_{NN}(\vec{q}) = \frac{1}{N} \langle \left| \sum_m e^{i\vec{q}\cdot\vec{R}_m} - N\delta_{\vec{q},o} \right|^2 \rangle$$

$$= 1 + \frac{1}{N} \langle \sum_{m\neq n} e^{i\vec{q}\cdot(\vec{R}_m - \vec{R}_n)} \rangle - N\delta_{\vec{q},o}$$

$$= 1 + \frac{1}{N} \int e^{i\vec{q}\cdot\vec{r}} \langle \sum_{m\neq n} \delta(\vec{r} - \vec{R}_m + \vec{R}_n) \rangle d^3r - N\delta_{q,o} \quad .$$

Hence

$$\frac{1}{V} \sum_q [S_{NN}(q) - 1] = -\frac{N}{V} + \frac{1}{N} \int \delta(\vec{r}) \langle \sum_{m\neq n} \delta(\vec{r} - \vec{R}_m + \vec{R}_n) \rangle d^3r \qquad (2.18)$$

where we have used the relation

$$\frac{1}{V} \sum_q e^{i\vec{q}\cdot(\vec{r}-\vec{r}')} = \frac{1}{(2\pi)^3} \int e^{i\vec{q}\cdot(\vec{r}-\vec{r}')} d^3q = \delta(\vec{r}-\vec{r}') \quad . \qquad (2.19)$$

The integral on the right-hand side of (2.18) is zero since R_m and R_n are positions of two distinct particles. Hence

$$\frac{1}{V} \sum_q [S_{NN}(\vec{q}) - 1] = -\frac{N}{V} \qquad (2.20)$$

or, in the integral form

$$\frac{1}{(2\pi)^3}\int[S_{NN}(\vec{q}) - 1]d^3q = -\frac{N}{V} \quad . \tag{2.21a}$$

Similarly one may show that

$$\int[S_{CC}(\vec{q}) - c(1-c)]d^3q = 0 \tag{2.21b}$$

$$\int S_{NC}(\vec{q})d^3q = 0 \quad . \tag{2.21c}$$

The corresponding sum rules for $a_{\alpha\beta}(q)$ were given by Enderby et. al. (1966). They may be immediately obtained from (2.21) and (2.16) as ($\alpha,\beta = 1,2$)

$$\frac{1}{(2\pi)^3}\int(a_{\alpha\beta}(q) - 1)d^3q = -\frac{N}{V} \quad , \tag{2.22}$$

for all the partial interference functions $a_{\alpha\beta}(q)$. Using (2.4), the corresponding sum rules for $S_{\alpha\beta}(q)$ are obvious and will be omitted here.

We observe from (2.21a) and (2.22) that $S_{NN}(\vec{q})$ satisfies the same sum rule as $a_{\alpha\beta}(\vec{q})$. In contrast, the sum rules (2.21b) and (2.21c), for $S_{CC}(\vec{q})$ and $S_{NC}(\vec{q})$ respectively, are different from that of $S_{NN}(\vec{q})$ and $a_{\alpha\beta}(\vec{q})$. These sum rules clearly imply that, for large q, all three $a_{\alpha\beta}(\vec{q})$ and $S_{NN}(\vec{q})$ oscillate about unity, whereas $S_{CC}(\vec{q})$ oscillates about c(1-c) and $S_{NC}(\vec{q})$ about zero.

Apart from the sum rules, each set of structure factors satisfies certain additional constraints. For the number-concentration structure factors, two of these follow from the definitions, namely that

$$S_{NN}(q) \geq 0 \quad \text{and} \quad S_{CC}(q) \geq 0 \; . \tag{2.23}$$

A further constraint can be deduced from the expression for the scattered intensity (in the weak scattering approximation). If $W_1(\vec{q})$ and $W_2(\vec{q})$ are the atom form factors (for electron, neutron or X-ray scattering), then the scattered intensity is essentially given by

$$I(\vec{q}) = [\bar{W}(\vec{q})]^2 S_{NN}(\vec{q}) + [\Delta W(\vec{q})]^2 S_{CC}(\vec{q}) + 2[\bar{W}(\vec{q})][\Delta W(\vec{q})] S_{NC}(\vec{q}) \tag{2.24}$$

where

$$\bar{W}(q) = cW_1(q) + (1-c)W_2(q) \quad \text{and} \quad \Delta W(q) = W_1(q) - W_2(q) \; . \tag{2.25}$$

If this expression is to be non-negative for all $W_1(q)$ and $W_2(q)$, then in addition to $S_{NN}(q) \geq 0$ and $S_{CC}(q) \geq 0$, we must have

$$S_{NN}(q) S_{CC}(q) - S_{NC}^2(q) \geq 0 \; . \tag{2.26}$$

In terms of the $a_{\alpha\beta}(\vec{q})$, the expression for $I(\vec{q})$ is given by [Faber and Ziman (1965)]

$$I(q) = c_1 W_1^2(q) + c_2 W_2^2(q) + c_1^2 W_1^2(q)[a_{11}(q)-1] +$$

$$+ c_2^2 W_2^2(q)[a_{22}(q)-1] + 2c_1 c_2 W_1(q) W_2(q)[a_{12}(q)-1] \ , \tag{2.27}$$

from which one may deduce that the $a_{\alpha\beta}(q)$ must satisfy the constraints [Enderby et. al. (1966), Faber (1972)],

$$c_1 a_{11}(q) + c_2 \geq 0$$

$$c_2 a_{22}(q) + c_1 \geq 0 \tag{2.28}$$

$$(c_1 a_{11}(q)+c_2)(c_2 a_{22}(q)+c_1) \geq c_1 c_2 [a_{12}(q)-1]^2 \ .$$

We note that individually the $a_{\alpha\beta}(q)$ may be either positive or negative.

2.3 Long Wavelength Limits of the Structure Factors

The properties of the structure factors discussed in the last section, namely the sum rules and the asymptotic behaviour for large q, are independent of the individual characteristics of a system. In contrast, the long wavelength ($q \to 0$) limits of the structure factors depend on the thermodynamic properties of the mixture. This thermodynamic connection is perhaps most transparent for the number-concentration structure factors and we consider them first.

It will be recalled that $S_{NN}(q)$ describes the correlation between the particle density and

particle density, irrespective of the concentrations. For a fluid, it then represents, in the $q \to 0$ limit, simply the mean square fluctuations in the total number of particles in the volume V of the medium

$$S_{NN}(q \to 0) \equiv S_{NN}(0) = \frac{\langle (\Delta N)^2 \rangle}{N} \quad . \tag{2.29}$$

Similarly

$$S_{CC}(0) = N\langle (\Delta c)^2 \rangle \ , \quad S_{NC}(0) = \langle \Delta N \Delta c \rangle \tag{2.30}$$

where $\langle (\Delta c)^2 \rangle$ is the mean square fluctuation in the concentration, Δc being defined by

$$\Delta c = N^{-1}[(1-c)\Delta N_1 - c\Delta N_2]$$

and $\langle \Delta N \Delta c \rangle$ is the correlation between the two fluctuations Δc and $\Delta N = \Delta N_1 + \Delta N_2$.

The expressions for the $S_{NN}(0)$ etc. may then be obtained straightforwardly from the fluctuation theory and one finds [Bhatia and Thornton (1970)],

$$S_{CC}(0) \equiv S_{CC}(q \to 0) = \frac{Nk_BT}{\left(\frac{\partial^2 G}{\partial c^2}\right)_{T,P,N}} \tag{2.31}$$

$$S_{NN}(0) \equiv S_{NN}(q \to 0) = \theta + \delta^2 S_{CC}(0) \tag{2.32}$$

$$S_{NC}(0) \equiv S_{NC}(q \to 0) = -\delta S_{CC}(0) \tag{2.33}$$

Here G is the Gibbs free energy, P is the pressure and δ is the dilatation factor

$$\delta = \frac{1}{V}\left(\frac{\partial V}{\partial c}\right)_{T,P,N} = \frac{v_1 - v_2}{c_1 v_1 + c_2 v_2} \quad , \tag{2.34}$$

where v_1 and v_2 are the partial molar volumes of the two species in the mixture. Finally,

$$\theta = \frac{N}{V} k_B T \kappa_T \tag{2.35}$$

where $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,c,N}$ is the isothermal compressibility at constant composition.

If the partial molar volumes of the two species are the same, then $\delta = 0$ and the fluctuations in number density are independent of those in concentration ($S_{NC}(0) = 0$), as might be expected intuitively. Further, $S_{NN}(0)$ is then θ, like the expression (1.1) for the structure factor of a pure liquid.

The expressions for the long wavelength limit of the other structure factors ($a_{ij}(q)$, $S_{ij}(q)$) follow immediately from the relations between these and $S_{NN}(q)$, etc. given in §2.1. Substituting (2.31)-(2.33) into (2.16), we have ($c_1 \equiv c$, $c_2 \equiv (1-c)$)

$$a_{11}(0) = \theta - \frac{c_2}{c_1} + \left(\frac{1}{c_1} - \delta\right)^2 S_{CC}(0)$$

$$a_{22}(0) = \theta - \frac{c_1}{c_2} + \left(\frac{1}{c_2} + \delta\right)^2 S_{CC}(0)$$

$$a_{12}(0) = \theta + 1 - \left(\frac{1}{c_1} - \delta\right)\left(\frac{1}{c_2} + \delta\right) S_{CC}(0) \quad . \tag{2.36}$$

Finally using (2.36) into (2.4), we have

$$S_{11}(0) = c_1\theta + c_1 S_{CC}(0)\left(\frac{1}{c_1} - \delta\right)^2$$

$$S_{22}(0) = c_2\theta + c_2 S_{CC}(0)\left(\frac{1}{c_2} - \delta\right)^2$$

$$S_{12}(0) = (c_1c_2)^{\frac{1}{2}}\theta - (c_1c_2)^{\frac{1}{2}} S_{CC}(0)\left(\frac{1}{c_1} - \delta\right)\left(\frac{1}{c_2} + \delta\right)^2. \qquad (2.37)$$

We thus see that the concentration dependence of the $q \to 0$ limit of the various structure factors are known if we know the volume V, the compressibility κ_T and the concentration fluctuations $S_{CC}(0)$ as functions of composition. The volume and κ_T, though not easily amenable to calculation, are directly measurable quantities. For $S_{CC}(0)$ we require the Gibbs free energy G as a function of c. We recall that G for a binary mixture can be quite generally written in the form

$$G = \mathcal{N}[cG_1^{(o)}(P,T) + (1-c)G_2^{(o)}(P,T)] + G_M \qquad (2.38)$$

where $\mathcal{N} = N/N_a$ (N_a is Avogadro's number†), $G_1^{(o)}$ and $G_2^{(o)}$ are the molar Gibbs free energies of the two pure

---

† In conformity with the standard thermodynamic usage we shall henceforth express the extensivity of G in terms of gm moles ($\mathcal{N}$) of the mixture rather than the total number of atoms (N).

species (at the pressure and temperature of the mixture) and G_M is the free energy of mixing (arising from the entropy and energy of mixing). Since $G_1^{(o)}$ and $G_2^{(o)}$ are by definition independent of concentration, we have from (2.37) and (2.31)

$$S_{CC}(0) = \frac{\mathcal{N}RT}{\left(\frac{\partial^2 G_M}{\partial c^2}\right)_{T,P,\mathcal{N}}} \qquad (2.39)$$

where $R = N_a k_B$ is the gas constant. Thus we have to know G_M as a function of the composition.

Theoretically, expressions for G_M are available in the literature for several models of the mixtures, e.g. the ideal solution, the regular solutions in zeroth and quasi-chemical approximations, athermal mixtures, etc. For reviews see, for example, Guggenheim (1952), Rowlinson (1969), Prigogine (1957). We examine the behaviour of the structure factors on the basis of some of these models in the next chapter. As already mentioned, the existing models do not in general suffice for systems which have, in the solid phase, a strong tendency to form compounds. A calculation of G_M and hence of $S_{CC}(0)$ etc. for the compound forming systems is described in Chapters 4 and 5.

$S_{CC}(0)$ can be calculated from the experimental data also, since the concentration dependence of G_M is

tabulated [for example, in Hultgren et. al. (1963)] for many molten alloys. Experimental G_M is inferred from the heat of mixing data as a function of temperature or, what is more common, from the activity data. The activity a_1 of component 1 in the mixture is defined by

$$RT \ln a_1 = \left(\frac{\partial G}{\partial \mathcal{N}_1}\right)_{T,P,\mathcal{N}_2} - G_1^{(o)}$$

$$= \left(\frac{\partial G_M}{\partial \mathcal{N}_1}\right)_{T,P,\mathcal{N}_2}$$

$$= \frac{1}{\mathcal{N}}\left(G_M + (1-c)\left(\frac{\partial G_M}{\partial c}\right)_{T,P,\mathcal{N}}\right) \qquad (2.40)$$

where $\mathcal{N}_1 = \mathcal{N}c$ is the number of gm moles of component 1 in the mixture, and $\mathcal{N}_2 = \mathcal{N}(1-c)$. The activity a_2 of component 2 is defined similarly. When the activities are known, it is actually not necessary to first integrate them to obtain G_M, since $S_{CC}(0)$ is related to a_1 or a_2 by [McAlister and Turner (1972), Ichikawa and Thompson (1973)]

$$S_{CC}(0) = \frac{(1-c)}{\dfrac{d \ln a_1}{dc}} = -\frac{c}{\dfrac{d \ln a_2}{dc}} , \qquad (2.41)$$

as may be readily verified from (2.39) and (2.40).

CHAPTER 3

CONCENTRATION FLUCTUATIONS AND PARTIAL STRUCTURE FACTORS IN IDEAL AND WEAKLY INTERACTING MIXTURES

3.1 Introduction

The thermodynamic relations given in the preceding chapter make it possible to carry out a systematic examination of the behaviour of the long wavelength limits of the structure factors for various types of mixtures. The present chapter is concerned with the study of concentration fluctuations S_{CC} and partial structure factors† a_{ij} for ideal (non-interacting) and weakly interacting mixtures. Prior to about 1970, it was generally held that the so-called substitutional hypothesis for $a_{ij}(q)$ might not be an unreasonable approximation. In this approximation $a_{ij}(q)$ are regarded as nearly independent of concentration and $a_{11}(q) \simeq a_{22}(q) \simeq a_{12}(q)$. In the paper giving the aforementioned

---

† In this chapter and Chapters 4 and 5, we shall be concerned with only the long wavelength limits of the structure factors. Hence we make the conventions: the words "in the long wavelength limit" are to be understood unless stated otherwise; also, the argument (0) in $S_{NN}(0)$ is deleted so that $S_{NN} \equiv S_{NN}(0)$, $a_{ij} \equiv a_{ij}(0)$ etc.

thermodynamic relations for the structure factors, Bhatia and Thornton (1970) showed, by an example, that while the substitutional hypothesis may well be reasonable for high q, it is far from justified in the $q \to 0$ limits. Subsequently McAlister and Turner (1972), using thermodynamic data, obtained a_{ij} for Na-K and K-Hg alloys and found them to be highly concentration dependent. It was therefore felt desirable to examine the behaviour of a_{ij} on the basis of some known theoretical models for mixtures.

The plan of the chapter is as follows.† In §3.2, S_{CC} and a_{ij} are described for the ideal solutions. In §3.3 we derive, for later use, some general formulae for a_{ij} in the low concentration limit. In §3.4, the regular solution model (in zeroth approximation - i.e. for weak interaction) is described and the expressions for S_{CC} and other structure factors are derived. Section 3.5 is devoted to the application of these formulae to Na-K alloy. Finally in §3.6, some remarks are made on concentration fluctuations in mixtures where the difference between the sizes of the atoms is so large that they cannot be regarded as regular solutions.

---

† The work on partial structure factors presented here was published in Bhatia, Hargrove and March (1973).

3.2 Ideal Solution

3.2.1 G_M, κ_T, δ and S_{CC}

The simplest type of mixture is the ideal solution for which the free energy of mixing G_M is just $(-T)$ times the entropy of random mixing, so that

$$(G_M)_{ideal} = \mathcal{N}RT\ [c\ \ell n\, c + (1-c)\ \ell n\ (1-c)] \qquad (3.1)$$

and hence from (2.38)

$$G = \mathcal{N}[cG_1^{(o)} + (1-c)G_2^{(o)}] + \mathcal{N}RT[c\ \ell n\ c + (1-c)\ell n(1-c)]. \qquad (3.2)$$

From (3.2) we have for the volume V of the mixture

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N,c} = \mathcal{N}\left[c\left(\frac{\partial G_1^{(o)}}{\partial P}\right)_T + (1-c)\left(\frac{\partial G_2^{(o)}}{\partial P}\right)_T\right]$$

$$= \mathcal{N}[cV_1^{(o)} + (1-c)V_2^{(o)}] \qquad (3.3)$$

where $V_1^{(o)}$ and $V_2^{(o)}$ are the molar volumes of the two pure species (at the same temperature and pressure as that of the mixture). Eqn. (3.3) expresses the well known Vegard's law regarding the linear variation of volume with concentration. Similarly

$$V\kappa_T = -\left(\frac{\partial V}{\partial P}\right)_{\mathcal{N},T,c} = -\left(\frac{\partial^2 G}{\partial P^2}\right)_{\mathcal{N},T,c} \qquad (3.4)$$

$$= \mathcal{N}[cV_1^{(o)}\kappa_T^{(1)} + (1-c)V_2^{(o)}\kappa_T^{(2)}] \qquad (3.5)$$

where

$$\kappa_T^{(i)} = - \left[\frac{1}{V_i^{(o)}} \left(\frac{\partial V_i^{(o)}}{\partial P} \right)_T \right]$$

is the isothermal compressibility of the pure species i. We note that $V\kappa_T$ and not κ_T varies linearly with c for the ideal solution.

Using (3.3) in (2.34), the expression for the dilatation factor δ becomes

$$\delta = \frac{1}{V} \left(\frac{\partial V}{\partial c} \right)_{T,P,\mathcal{N}} = \frac{V_1^{(o)} - V_2^{(o)}}{cV_1^{(o)} + (1-c)V_2^{(o)}} \quad . \tag{3.6}$$

The variation of δ with c according to (3.6) is illustrated in Fig. 3.1 for two values of $V_2^{(o)}/V_1^{(o)}$.

Finally substituting (3.1) in (2.39) we have for the concentration fluctuations

$$S_{CC}^{id} = c(1-c) \ , \tag{3.7}$$

where the superscript 'id' has been added to signify that this is the expression for S_{CC} for an ideal solution.

3.2.2 Partial Structure Factors

With S_{CC} given by (3.7), the expressions (2.36) for a_{ij} become ($c_1 \equiv c$, $c_2 \equiv 1-c$)

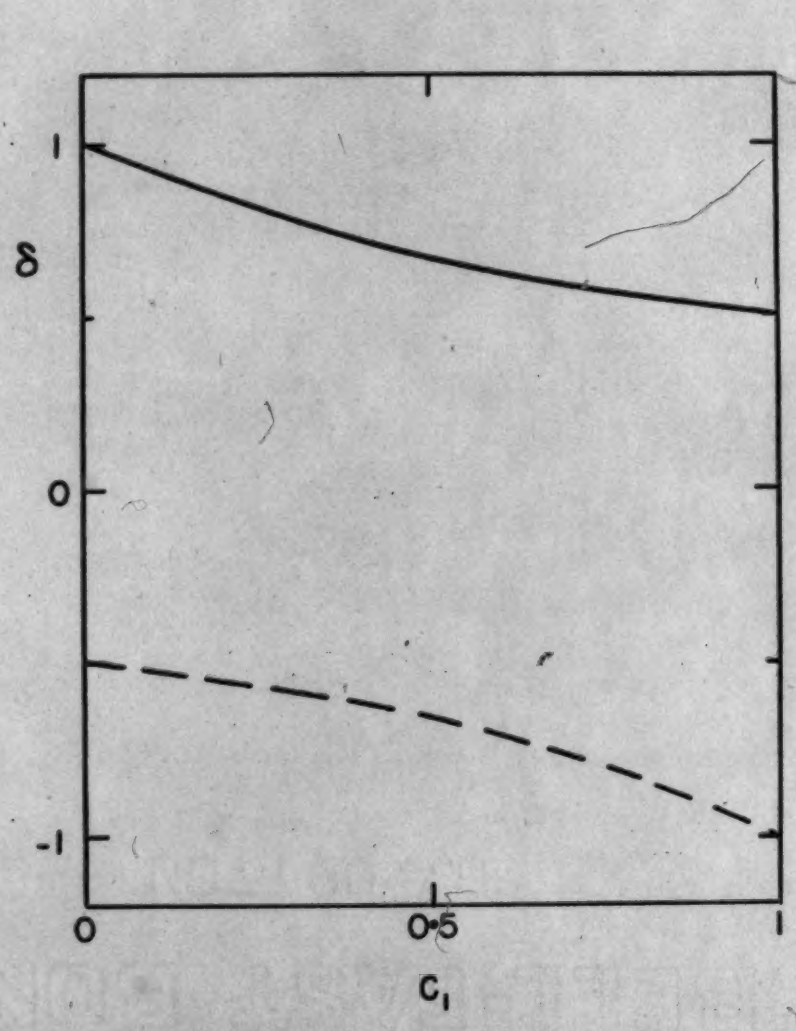

Fig. 3.1. Variation of dilatation factor δ with concentration for a mixture obeying Vegard's law. —— $\beta = V_1^{(o)}/V_2^{(o)} = 2$, – – $\beta = 1/2$.

$$a_{11} = \theta - 2c_2\delta + c_1c_2\delta^2$$

$$a_{22} = \theta + 2c_1\delta + c_1c_2\delta^2$$

$$a_{12} = \theta + \delta(c_1-c_2) + c_1c_2\delta^2 \quad , \qquad (3.8)$$

we observe that if the mixture, in addition to being ideal, is such that $\delta = 0$ (i.e. the two pure species have the same molar volumes), then the substitutional hypothesis is valid, that is,

$$a_{11} = a_{22} = a_{13} = \theta \quad . \qquad (3.9)$$

Usually θ is no more than 0.03-0.05 at the melting point of an alloy and in Figs. 3.2 and 3.3 we sketch, taking $\theta = 0$, the variation of a_{ij} with c for the two sets of δ given in Fig. 3.1

3.3 Partial Structure Factors in the Low Concentration Limit

Before considering the behaviour of the partial structure factors for a non-ideal mixture on the basis of a model, it is useful to consider their general form at small concentrations.

In the $c \to 0$ limit, the mixture approaches the pure species 2. Since the leading term in S_{CC}, for

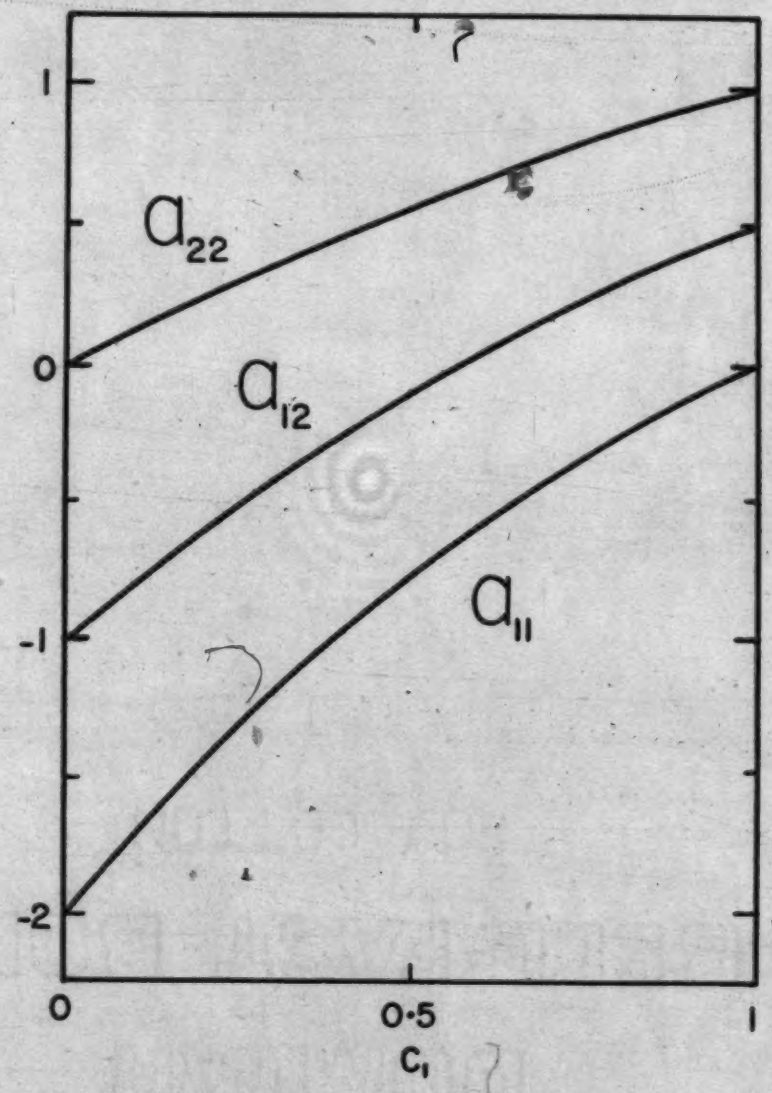

Fig. 3.2. Variation of a_{ij} with concentration in an ideal solution taking $\theta = 0$ and $\beta = V_1^{(o)}/V_2^{(o)} = 2$.

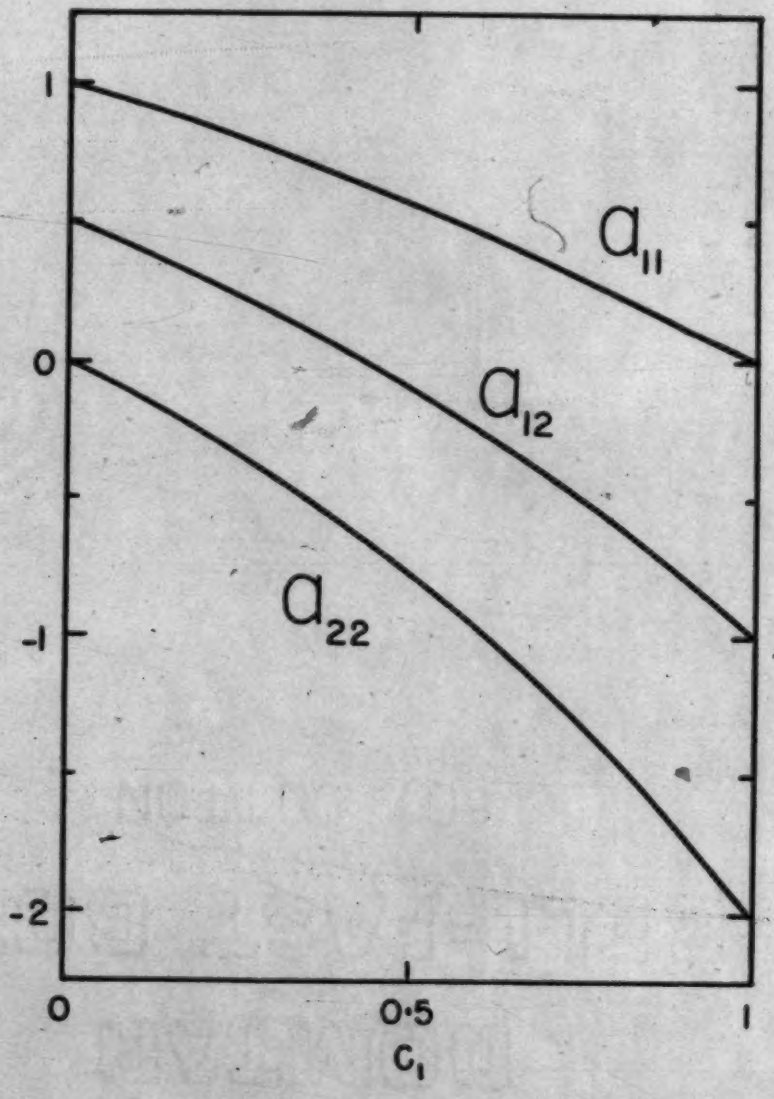

Fig. 3.3. Variation of a_{ij} with concentration in an ideal solution taking $\theta = 0$ and $\beta = 1/2$.

small c, is always† c, it follows from expressions (2.36) for a_{ij} that as $c \to 0$ ($c \equiv c_1$),

$$a_{22}^{o} = \theta^{o} \quad , \qquad a_{12}^{o} = \theta^{o} - \delta^{o}$$

and

$$a_{11}^{o} = \theta^{o} - 2\delta^{o} + \tfrac{1}{2}[(S''_{CC})_{c=0} + 2] \quad , \tag{3.10}$$

where the superscript 'o' means the value of the corresponding quantity is evaluated at c = 0. The expressions for a_{22}^{o} and a_{12}^{o} are the same as obtained by McAlister and Turner (1972), but their expression for a_{11}^{o} is $a_{11}^{o} = \theta^{o} - 2\delta^{o}$, which is true only for an ideal solution for which $[(S''_{CC})_{c=0} + 2] = 0$. Similarly, as $c \to 1$

$$a_{11}^{1} = \theta^{1} \quad , \qquad a_{12}^{1} = \theta^{1} + \delta^{1}$$

$$a_{22}^{1} = \theta^{1} + 2\delta^{1} + \tfrac{1}{2}[(S''_{CC})_{c=1} + 2] \quad . \tag{3.11}$$

For an <u>ideal</u> solution,

$$\delta^{o} = \beta - 1 \quad , \quad \delta^{1} = 1 - \beta^{-1} \quad , \quad \beta = \frac{V_1^{(o)}}{V_2^{(o)}} \tag{3.12}$$

and, from (3.10) and (3.11),

---

† For a dilute solution ($c \ll 1$), G_M has the form

$$G_M = \mathcal{N} RT[c \ln c + \alpha_1 c + \alpha_2 c^2 + \ldots]$$

the leading term (c ln c) resulting from entropy of mixing, must always be there. Hence, using (2.39) one has $S_{CC} \to c$ as $c \to 0$.

$$a_{12}^{o} = \theta^{o} - (\beta-1) \ , \quad a_{12}^{1} = \theta^{1} + (1-\beta^{-1}) \ . \qquad (3.13)$$

Also, from (3.8) and (3.12)

$$a_{22} \simeq \theta + c(\beta^2 - 1) \qquad \text{for } c \ll 1$$

and

$$a_{11} \simeq \theta + (1-c)(\beta^{-2} - 1) \quad \text{for } (1-c) \ll 1. \qquad (3.14)$$

It is interesting to note that if we set $\theta = 0$ in (3.13) and (3.14) and identify the volume ratio β as $(\sigma_1/\sigma_2)^3$, where σ_1 and σ_2 are the hard sphere diameters for the two types of atoms, then (3.13) and (3.14) reduce to those obtained by Faber (1972) using the hard sphere model. [Note the difference in notation and also that there is a misprint in Eqns. (6.17) and (6.18) of Faber (1972)]. Finally we see from (2.36) that the combination $a_{11} + a_{22} - 2a_{12}$ is independent of δ and θ and is given by

$$a_{11} + a_{22} - 2a_{12} = \frac{S_{cc} - c(1-c)}{[c(1-c)]^2} \ . \qquad (3.15)$$

This is zero for an ideal solution, and a non-zero value of it is a direct indication of non-ideality of the solution. If we represent, for small c, the departure from ideality by

$$S_{cc} \simeq c - c^2 + \mathcal{A} c^2 \ , \quad c \ll 1 \ , \qquad (3.16)$$

then

$$a_{11}^{o} + a_{22}^{o} - 2a_{12}^{o} = \mathcal{A} \ . \qquad (3.17)$$

We shall see presently that for regular solutions (in the zeroth approximation), $\mathcal{A}$ is a direct measure of an interchange energy in suitable units.

3.4 Regular Solutions in the Zeroth Approximation

3.4.1 Expression for the Free Energy

For a solution to be ideal, two conditions have to be satisfied: (a) the difference in the sizes of the two types of atoms must be small - in terms of the volume ratio β or $(\sigma_1/\sigma_2)^3$, it is usually considered sufficient if $\frac{1}{2} < \beta < 2$ [see, for example, Guggenheim (1952)]; (b) the difference ω in the pairwise interaction energies between the atoms must be zero (see below). In the regular solution theory the assumption (a) is retained, but the difference ω is considered to be non-zero.

When $\omega \neq 0$, only approximate expressions for the free energy of mixing G_M can be derived. The simplest approximation to G_M, which is valid when ω can be considered to be small (see below), is usually referred to as the "zeroth or Bragg-Williams approximation" (Guggenheim, 1952). The expression for the free energy of a regular solution in the "zeroth approximation" is usually derived in the following manner (e.g. see Guggenheim, 1952).

One assumes that the interaction is significant only between atoms which are nearest neighbours of one another. Let χ_{AA}, χ_{BB} and χ_{AB} denote, respectively, the interaction energies between nearest neighbour A-A, B-B and A-B atom pairs†, and let the number of nearest neighbours of each atom be Z. Then if N_{AA}, N_{BB} and N_{AB} denote the number of nearest neighbour A-A, B-B and A-B pairs in the mixture, the energy E of the solution is

$$E = N_{AA}\chi_{AA} + N_{BB}\chi_{BB} + N_{AB}\chi_{AB} \tag{3.18}$$

with

$$N_{AA} + N_{BB} + N_{AB} = \frac{1}{2} NZ = \frac{1}{2} \mathcal{N} N_a Z \ , \tag{3.19}$$

N being again the total number of atoms in the solution. If we now assume that the two types of atoms are distributed completely at random, then of the Z neighbours of a <u>given</u> atom, a fraction c will be A atoms and (1-c) B atoms. Hence ($c \equiv c_A$)

$$N_{AA} = \frac{1}{2} NZc^2 \ , \quad N_{BB} = \frac{1}{2} NZ\ (1-c)^2 \ ,$$

$$N_{AB} = 2(\tfrac{1}{2} NZ)\ c(1-c) \ . \tag{3.20}$$

---

† For convenience of writing two types of atoms will sometimes (as here) be also denoted by A and B with A ≡ species 1, B ≡ species 2.

Substituting (3.20) in (3.18) and rearranging terms

$$E = (\tfrac{1}{2}\mathcal{N}N_a z)[c^2\chi_{AA} + (1-c)^2\chi_{BB} + 2c(1-c)\chi_{AB}]$$

$$= \mathcal{N}\omega c(1-c) + \tfrac{1}{2}(\mathcal{N}N_a z)[c\chi_{AA} + (1-c)\chi_{BB}] \qquad (3.21)$$

where

$$\omega = (\tfrac{1}{2}N_a z)(2\chi_{AB} - \chi_{AA} - \chi_{BB}) \ . \qquad (3.22)$$

Since the terms in the square brackets are the appropriate linear (in c) combination of the characteristic energies of the pure constituents, the energy of mixing E_M is simply

$$E_M = \mathcal{N}\omega c(1-c) \ . \qquad (3.23)$$

Finally, since the atoms have been assumed to be at random, the contribution to G_M from the entropy of mixing is the same as for an ideal solution. Hence†

---

† We note that this expression for G_M is the same as that for the conformal solution model [Longuet-Higgins (1951)]. Here one assumes that the properties of the mixture can be described by small perturbations from a suitably chosen standard reference liquid (at the same temperature and pressure as the mixture). The word "conformal" refers to the fact that the interatomic potentials for the different pairs are assumed to have the same functional form. The two models are valid essentially under the same conditions, namely the assumption (a) and smallness of ω.

$$G_M = E_M + (G_M)_{ideal}$$

$$= \mathcal{N}RT[c \ln c + (1-c)\ln(1-c)] + \mathcal{N}\omega c(1-c) \quad (3.24)$$

and

$$G = \mathcal{N}cG_1^{(o)} + \mathcal{N}(1-c)G_2^{(o)} + \mathcal{N}RT[c\ln c + (1-c)\ln(1-c)]$$

$$+ \mathcal{N}\omega c(1-c) , \quad (3.25)$$

which are the desired expressions for G_M and G for a regular solution in the zeroth approximation.

The quantity ω, assumed to be concentration independent, is called the interchange energy. If we replace an AA pair and a BB pair by two AB pairs, then the energy of the mixture is increased by $[\omega/(\frac{1}{2} N_a Z)]$. Clearly if ω is positive the formation of like atom (nearest neighbour) pairs is energetically preferred over that of unlike atom pairs. The opposite is the case if ω is negative. This tendency of an atom to prefer one type of atom over another as its nearest neighbour was neglected in the above treatment when we assumed the atoms to be distributed completely at random. A somewhat better approximation is the so-called quasi-chemical approximation. Here it is found that the various types of pairs obey a sort of chemical equilibrium relation, namely,

$$\frac{N_{AA}N_{BB}}{(\frac{1}{2}N_{AB})^2} = e^{\frac{\omega}{\frac{1}{2}N_a Z k_B T}} = e^{2\omega/(ZRT)} , \qquad (3.26)$$

in contrast to (from (3.20))

$$\frac{N_{AA}N_{BB}}{(\frac{1}{2}N_{AB})^2} = 1 \qquad (3.27)$$

in the "zeroth approximation". Since the quasi-chemical approximation is itself approximate and quite complex†, we shall not pursue it here.

A comparison of (3.26) and (3.27) shows that the "zeroth approximation" should be valid if $|2\omega/(ZRT)| << 1$. If we say, somewhat arbitrarily, that the approximation should be valid for $|2\omega/ZRT| < \frac{1}{2}$, then since $Z \sim 8$, 10, we get a rough criterion for the "zeroth approximation" to be reasonable as

$$-2 < \frac{\omega}{RT} < 2 \quad . \qquad (3.28)$$

Since $|G_M|$, given by expression (3.24), is maximum at $c = \frac{1}{2}$, the condition (3.28) implies that

$$-1.2 < \frac{G_M}{\mathcal{N}RT} < -0.2 , \quad (\text{at } c = \tfrac{1}{2}) . \qquad (3.29)$$

We shall need (3.28) and (3.29) in our discussions later.

---

† For reviews see, for example, Guggenheim (1952) and Prigogine (1957).

3.4.2 Expressions for V, δ, κ_T and S_{CC}

With G given by (3.25), one obtains for the volume, δ and κ_T the expressions:

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,\mathcal{N},c} = \mathcal{N}\left[cV_1^{(o)} + (1-c)V_2^{(o)} + \alpha' V_1^{(o)} c(1-c)\right] \quad (3.30)$$

$$\delta = \frac{1}{V}\left(\frac{\partial V}{\partial c}\right)_{T,P,\mathcal{N}} = \frac{V_1^{(o)} - V_2^{(o)} + \alpha' V_1^{(o)}(1-2c)}{cV_1^{(o)} + (1-c)V_2^{(o)} + \alpha' V_1^{(o)} c(1-c)} \quad (3.31)$$

and

$$V\kappa_T = -\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,c,\mathcal{N}}$$

$$= \mathcal{N}\left(cV_1^{(o)}\kappa_T^{(1)} + (1-c)V_2^{(o)}\kappa_T^{(2)} + \alpha'' V_1^{(o)}\kappa_T^{(1)} c(1-c)\right) \quad (3.32)$$

where α' and α'' are dimensionless quantities proportional to the first and second derivatives of the interchange energy ω with respect to pressure

$$\alpha' = \frac{1}{V_1^{(o)}}\left(\frac{d\omega}{dP}\right)_T \quad , \quad \alpha'' = -\frac{1}{V_1^{(o)}\kappa_T^{(1)}}\left(\frac{d^2\omega}{dP^2}\right)_T \quad . \quad (3.33)$$

If ω is independent of pressure, V and $V\kappa_T$ are linear in concentration as for an ideal solution.

Using (3.24) in (2.39) one has for the concentration fluctuations:

$$S_{CC} = \frac{\mathcal{N}RT}{\left(\frac{\partial^2 G}{\partial c^2}\right)_{\mathcal{N},T,P}} = \frac{c(1-c)}{1 - \frac{2\omega}{RT}c(1-c)} \quad . \quad (3.34)$$

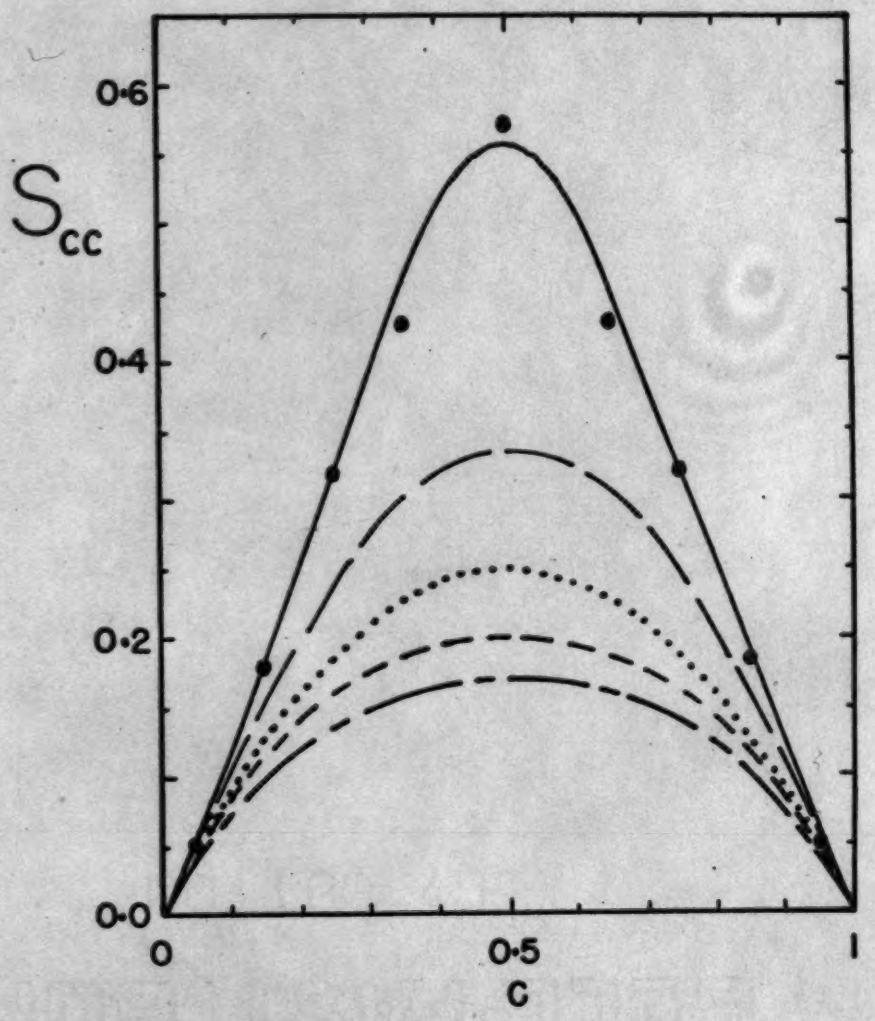

Fig. 3.4. Variation of S_{CC} with concentration for regular solutions in the zeroth approximation; ——— $\omega/RT = 1.1$, — — $\omega/RT = 0.5$, ... $\omega/RT = 0$ (ideal solution), --- $\omega/RT = 0.5$, ——— - ———- $=\omega/RT = -1.0$, ● data for Na-K from Hultgren et al. (1963).

We observe that S_{CC} is symmetric about $c = \frac{1}{2}$ and lies above the ideal value [$S_{CC}^{id} = c(1-c)$] if ω is positive and below it if ω is negative. If ω is positive, the solution has a critical point of mixing, the critical temperature T_{cm} being given by

$$T_{cm} = \frac{1}{2}\frac{\omega}{R} \quad . \tag{3.35}$$

Near this point S_{CC} becomes very large. Although the expression (3.24) for the free energy is too simple to adequately describe partially miscible liquids†, and the thermodynamic theory of fluctuations breaks down near the critical point, the largeness of the concentration fluctuations near T_{cm} is of course well known from the phenomena of critical opalescence in light scattering and other scattering experiments near $q = 0$.

Fig. 3.4 illustrates the variation of S_{CC} with concentration for a few values of ω/RT.

3.4.3 Expressions for the Partial Structure Factors

By combining (3.34) with (2.36), one immediately obtains

---

† As discussed near (3.28), for $|\omega|/RT \geq 2$, the zeroth approximation is likely to be poor whether ω is positive or negative.

$$a_{11} = \theta + X(\delta^2 c(1-c) - 2\delta(1-c) + \frac{2\omega}{RT}(1-c)^2)$$

$$a_{22} = \theta + X(\delta^2 c(1-c) + 2\delta c + \frac{2\omega}{RT} c^2)$$

and

$$a_{12} = \theta + X(\delta^2 c(1-c) - (1-2c)\delta - \frac{2\omega}{RT} c(1-c)) \qquad (3.36)$$

where we have set

$$X = \frac{S_{CC}}{c(1-c)} = \frac{1}{1 - (\frac{2\omega}{RT})c(1-c)} \quad . \qquad (3.37)$$

If we take the limit $c \to 0$ ($c \equiv c_1$), then

$$a_{11}^{o} = \theta^{o} - 2\delta^{o} + \frac{2\omega}{RT}$$

$$a_{22}^{o} = \theta^{o}$$

and

$$a_{12}^{o} = \theta^{o} - \delta^{o} \quad , \qquad (3.38)$$

yielding

$$a_{11}^{o} + a_{22}^{o} - 2a_{12}^{o} = \frac{2\omega}{RT} \qquad (3.39)$$

and showing that $\mathcal{A}$ in Eqn. (3.17) is simply related to the interchange energy ω in units of RT. The left-hand side is zero if $\omega = 0$, in agreement with the result in (3.15) that for an ideal solution $a_{11} + a_{22} - 2a_{12} = 0$. When $\omega \neq 0$, this combination of a_{ij} is given by the expression

$$a_{11} + a_{22} - 2a_{12} = \left(\frac{2\omega}{RT}\right) X$$

$$= \frac{2\omega/RT}{1 - c(1-c)\left(\frac{2\omega}{RT}\right)} \quad . \qquad (3.40)$$

Its variation with concentration is illustrated in Fig. 3.5.

3.5 Application of Regular Solution Theory to Na-K

3.5.1 Comparison with Experiment for S_{CC}, V and κ_T

For the Na-K alloy the data at 300°K on G_M and activities are given in Hultgren et. al. (1963). Within experimental errors G_M is symmetric about $c = \frac{1}{2}$ and at $c = \frac{1}{2}$ and $\frac{G_M}{\mathcal{N}RT} \simeq -0.43$ so that the regular solution theory as described above should be valid. The determination of S_{CC} from theory just requires one parameter, namely the interchange energy ω. Choosing ω so that $G_M/\mathcal{N}NT$ agrees with experimental at $c = \frac{1}{2}$, one finds

$$\omega/RT = 1.1 \ , \qquad T = 298.15°K \ .$$

With this value of ω the plot of S_{CC} against c is given in Fig. 3.4. As described in §2.3, the experimental values of S_{CC} are most readily determined by differentiating the activity data. We see from the Figure that the agreement between theory and experiment is fairly good.

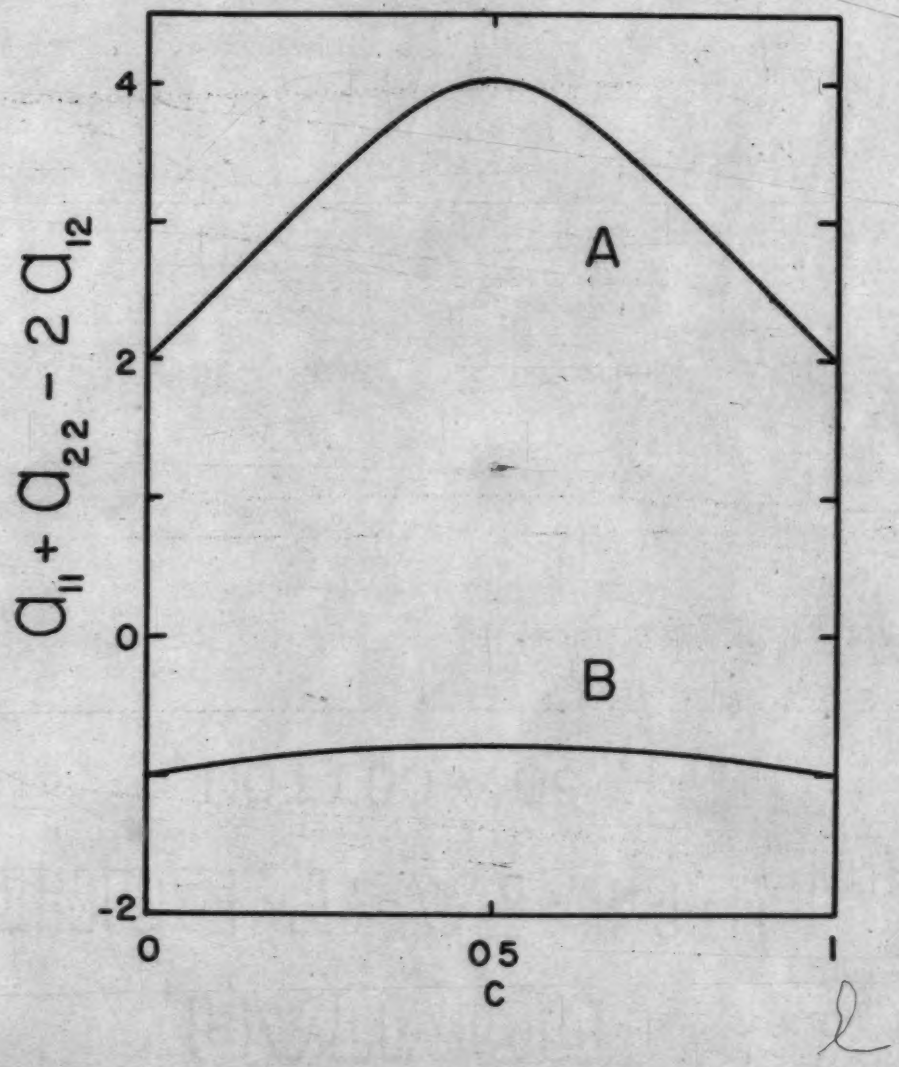

Fig. 3.5. Variation of $a_{11}+a_{22}-2a_{12}$ with concentration according to eq. (3.40).
A: $\omega/Rt = 1$; B: $\omega/RT = -1/2$.

For calculating V and κ_T as a function of concentration, one needs, apart from the volume and compressibility of the two pure species, the first and second pressure derivatives of ω, i.e. α' and α'' defined in (3.33). A theoretical calculation of these, as of ω itself, is a difficult problem and we regard here α' and α'' also as parameters. Using the observed volumes and compressibilities for pure Na and K, Figs. 3.6 and 3.7 illustrate the variation of V and $V\kappa_T$ with concentration c for several values of α' and α''. The curve with $\alpha' = -0.1$ for volume and the curve with $\alpha'' = -0.5$ for $V\kappa_T$ fit quite well with the respective data on these quantities due to Abowitz and Gordon (1962). Thus we see that for the Na-K system the departures from linearity are quite small. How these small departures affect δ is depicted in Fig. 3.8.

3.5.2 Partial Structure Factors

Once S_{CC}, V and κ_T, and hence δ and θ are known, it is an easy matter to evaluate a_{ij} using (3.36). From the values of V and κ_T for the Na-K system given in the preceding section, one finds that θ $[=(N/V)RT\kappa_T]$ lies between 0.05 and 0.0 in the entire concentration range and makes negligible contribution to a_{ij} at most concentrations. Fig. 3.9 depicts the variation

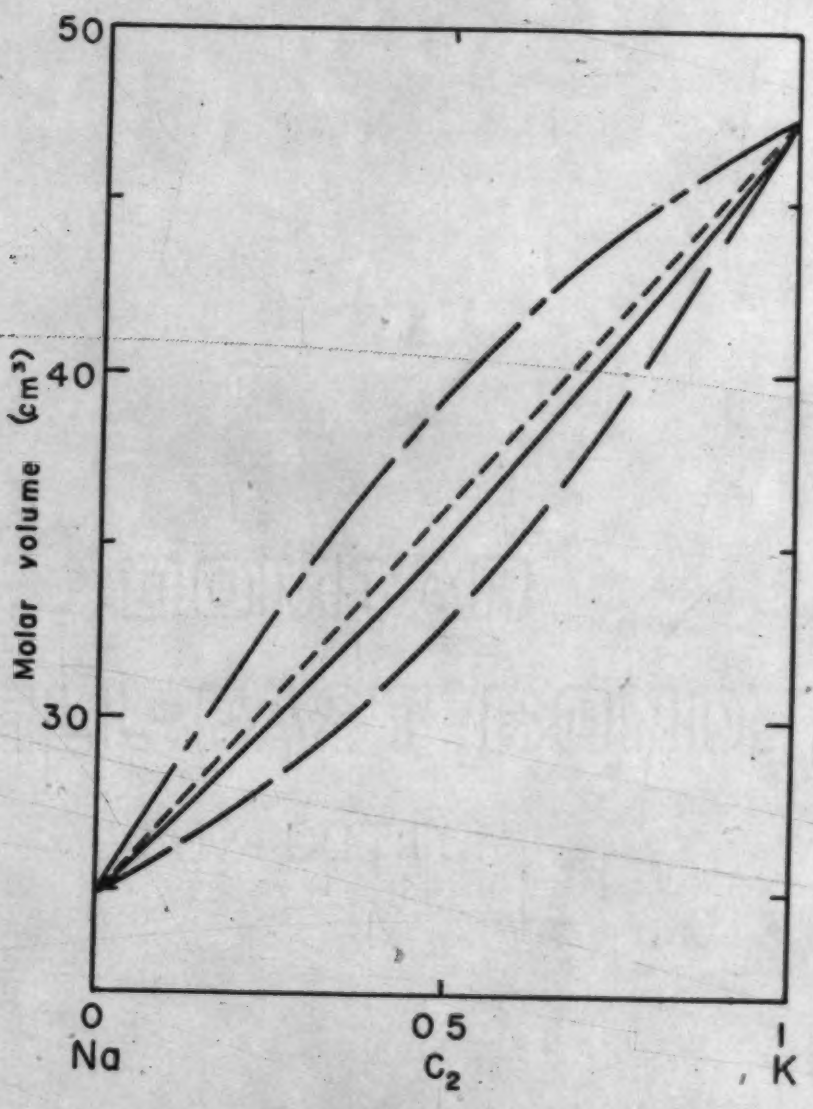

Fig. 3.6. Molar volume against potassium concentration for Na-K alloys at 100°C:
—— —— α' = -0.5, ———— α' = -0.1,
----- α' = 0, —— - —— - α' = 0.5.

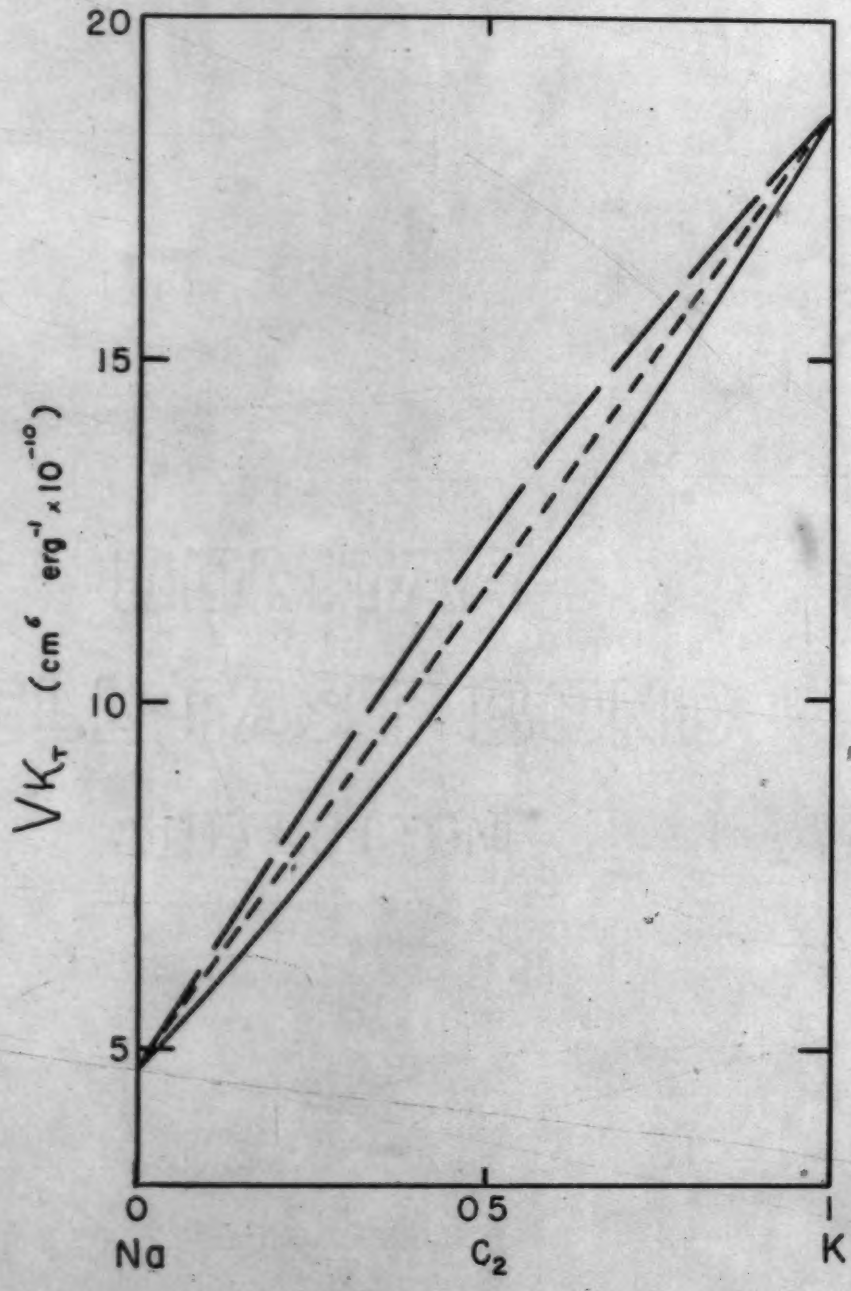

Fig. 3.7. Volume times compressibility against potassium concentration for Na-K alloys at 100°C: ——— $\alpha'' = -0.5$, ----- $\alpha'' = 0$, — — — $\alpha'' = 0.5$.

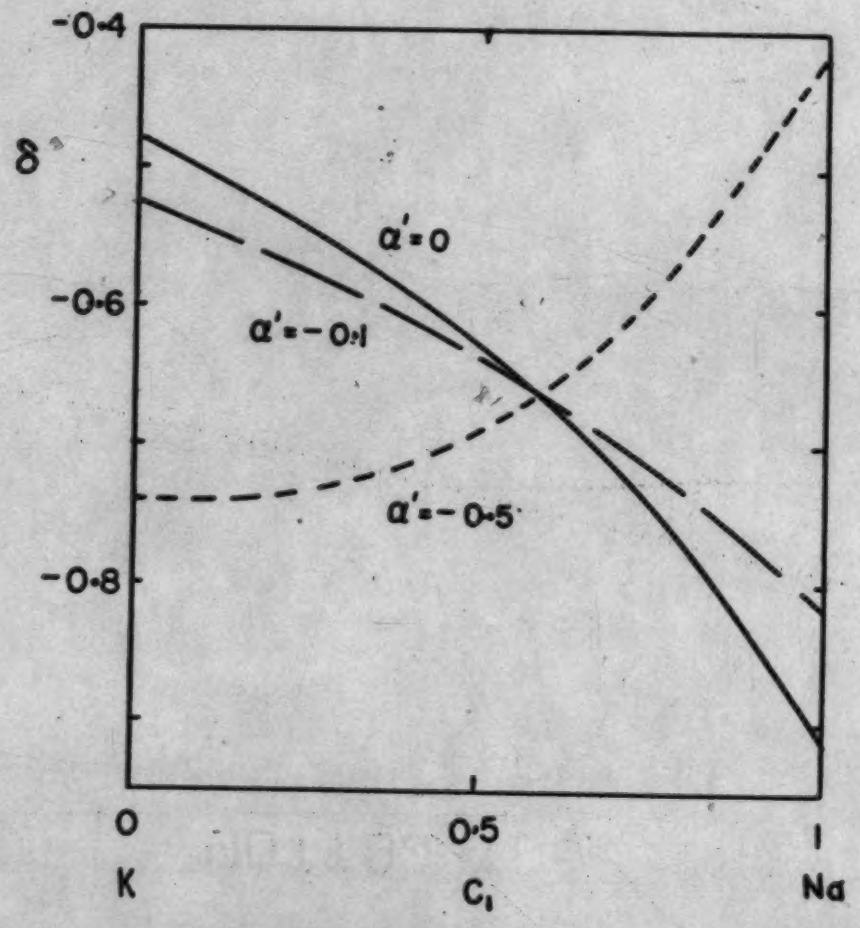

Fig. 3.8. Dilatation factor δ versus sodium concentration for Na-K alloys for several values of α'.

of a_{ij} with concentration for the parameters α', α'' and ω appropriate to Na-K system. Since as discussed above V and $V\kappa_T$ vary approximately linearly with c, the curves taking $\alpha' = \alpha'' = 0$ are also given. We see that, as expected, the two sets of curves lie very close to each other.

Fig. 3.9 also gives the experimental values of a_{ij} obtained by McAlister and Turner (1972). It will be seen that the agreement with theory is good except for a_{11} ($\equiv a_{NaNa}$) near c_1 ($\equiv c_{Na}$) = 0 and for a_{22} ($\equiv a_{KK}$) near $c_1 = 1$. This discrepancy is due to the fact that, as discussed in §3.2, they determined a_{11}^o (value of a_{11} at $c_1 = 0$) by substituting the observed values of θ and δ in the formula

$$a_{11}^o = \theta^o - 2\delta^o \qquad (3.41a)$$

which is only appropriate if $S_{CC} = S_{CC}^{id}$, rather than the expression (3.10), which for our model gives [from (3.38)]

$$a_{11}^o = \theta^o - 2\delta^o + \frac{2\omega}{RT} \ . \qquad (3.41b)$$

The values of a_{11}^o from (3.41a) and (3.41b) are respectively 0.7 and 2.9 at 100°C. The use of the latter value for a_{11}^o would remove the sudden drop near $c_1 = 0$ in the experimental curve for a_{11}, thus bringing it close to the theoretical curve. Similar remarks of

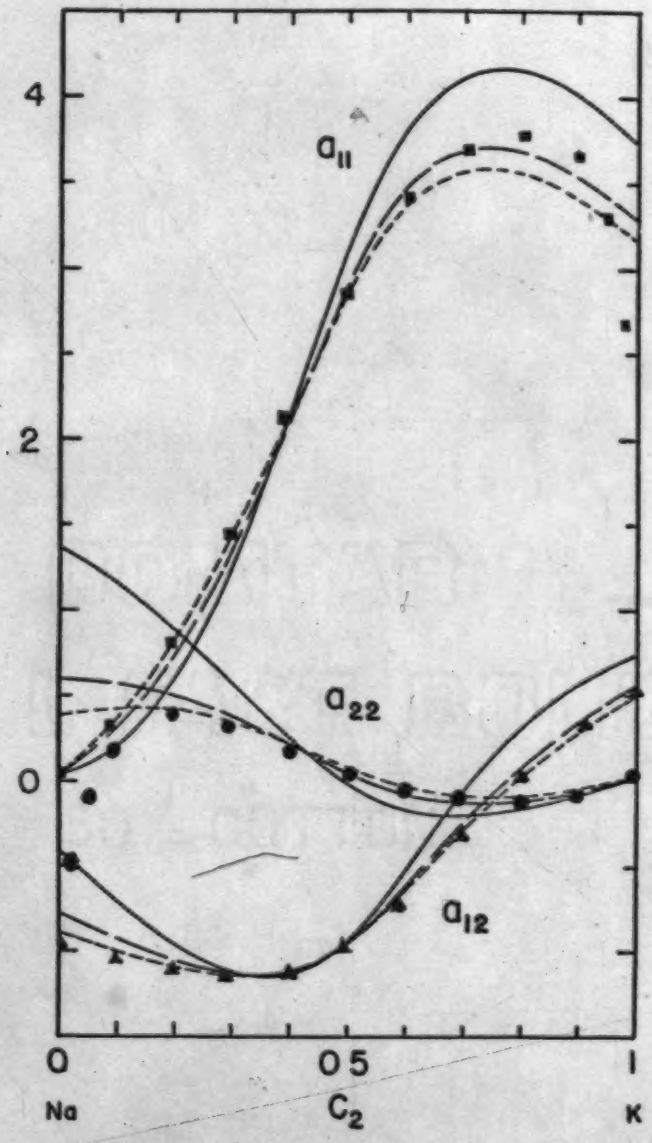

Fig. 3.9. Variation of a_{ij} with concentration for Na-K alloys at 100°C. ——— $\alpha' = -0.1$, $\alpha'' = -0.5$; ----- $\alpha' = 0$, $\alpha'' = 0$; ——————— $\alpha' = -0.5$, $\alpha'' = 0.5$; ■, ●, ▲ experimental from McAlister and Turner (1972).

course apply to a_{22} near $c_1 = 1$, the two values of a_{22}^1 now being

$$a_{22}^1 = \theta^1 + 2\delta^1 \simeq -1.95$$

and

$$a_{22}^1 = \theta^1 + 2\delta^1 + \frac{2\omega}{RT} \simeq 0.25 \ .$$

3.5.3 Concluding Remarks

To conclude, we see firstly that for the Na-K system the a_{ij} vary markedly with concentration and that their values are in general very different from $a_{ij} \simeq \theta$ expected from the substitutional hypothesis. Secondly, we have shown that the regular solution model in the zeroth approximation is capable of explaining all the data for this system. For K-Hg alloy also (the other system examined by McAlister and Turner), the a_{ij} vary strongly with concentration. We cannot however apply the above model to this system since the magnitude of the observed free energy of mixing

$$\frac{G_M}{\mathcal{N}RT} \simeq -3.3 \quad \text{at} \quad c \simeq 0.4 \ , \quad T = 600°K \ ,$$

in conjunction with (3.29) shows that this is not a weakly interacting system. Also, the volume ratio β $(= V_K^{(o)}/V_{Hg}^{(o)} \simeq 3)$ is large. We shall consider this system in the next chapter.

3.6 Effect of Size Difference on Concentraction Fluctuations in Weakly Interacting Systems

We conclude this chapter by briefly discussing, for the sake of completeness, the behaviour of concentration fluctuations S_{CC} in a system for which, though the interchange energy ω is small, the difference in volumes of the two species is too large for the regular solution model to apply. For such a system a more valid approximation, in a similar vein to (3.24), is Flory's formula [Flory (1953), Guggenheim (1952)],

$$G_M = \mathcal{N}RT\{[c\ \ell n\,\phi + (1-c)\ell n(1-\phi)]\} + \{\mathcal{N}\omega\phi(1-\phi)[c+(1-c)/\beta]\} \qquad (3.42)$$

where, as before, ω is a suitably defined interchange energy, while ϕ is the concentration of species 1 by volume and β is the volume ratio. With ω independent of pressure, as is usually assumed when using this approximation,

$$\phi = \frac{cV_1^{(o)}}{cV_1^{(o)} + (1-c)V_2^{(o)}}, \qquad \beta = \frac{V_1^{(o)}}{V_2^{(o)}} . \qquad (3.43)$$

From (3.42) and (2.39) we have

$$S_{CC} = \frac{c(1-c)}{1 + c(1-c)\delta^2\left[1 - \frac{2\beta\delta\omega}{(\beta-1)^3 RT}\right]}, \qquad (3.44)$$

where

$$\delta = \frac{V_1^{(o)} - V_2^{(o)}}{cV_1^{(o)} + (1-c)V_2^{(o)}} = \frac{\beta - 1}{(1-c) + c\beta} \quad . \qquad (3.45)$$

We see from (3.44) that, unlike the case of regular solutions (δ small), $S_{CC}(0)$ now also depends on δ. In particular, even for an athermal mixture, i.e. when the interchange energy $\omega = 0$, S_{CC} is not just equal to $c(1-c)$ as for a truly random (ideal) solution. The variation of S_{CC} for several values of ω/RT, for the case $\beta = \frac{1}{3}$, is illustrated in Fig. 3.10.

We should finally mention again that (3.42), like (3.24) for the regular solutions, is valid only for weakly interacting systems with restrictions on G_M similar to (3.29). Also, we should note that although Flory's expression does indeed reduce, for $\beta = 1$, to the "regular solution" expression (3.24), it should probably be viewed to be valid only for about $\beta \gtrsim 2$ or $\beta \lesssim \frac{1}{2}$.

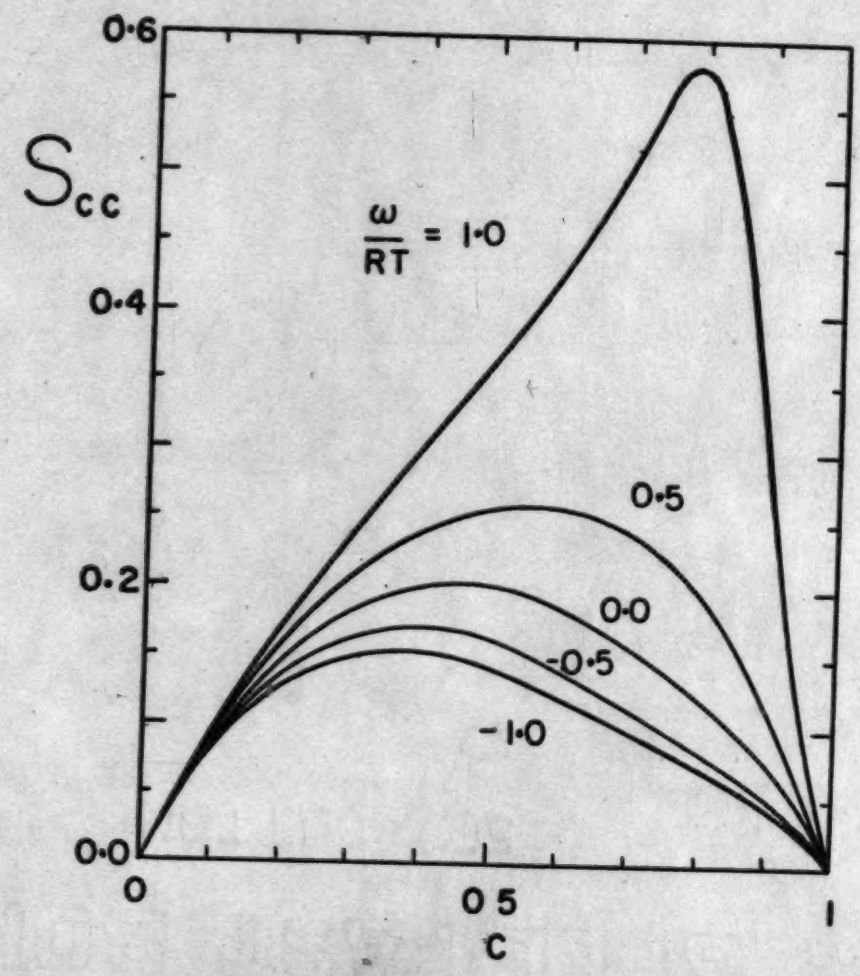

Fig. 3.10. Variation of S_{CC} with concentration in Flory's approximation (eq. (3.44)) for the volume ratio $\beta = 1/3$ and several values of ω/RT (Fig. from Bhatia and March (1975)).

CHAPTER 4

CONCENTRATION FLUCTUATIONS AND PARTIAL STRUCTURE FACTORS OF COMPOUND FORMING BINARY MOLTEN ALLOYS

4.1 Introduction and Model

In the preceding chapter, we discussed the behaviour of the concentration fluctuations S_{CC} and other structure factors on the basis of some simple theoretical models of mixtures. Basically this discussion was applicable to systems in which the difference ω in the pairwise interaction energies between the two species can be considered to be small (see Eqns. (3.28) and (3.29)). There is, however, an interesting class of molten systems - examples being K-Hg (already mentioned in Chapter 3), Mg-Bi, Tl-Te, etc. - where this difference is not small. This is evidenced by the fact, amongst others (magnitude of $G_M/\mathcal{N}RT$ etc.), that in the solid phase they form intermetallic compounds at one or more well defined stoichiometric compositions. In this and the next chapter we discuss, using a phenomenological model, some characteristic features of S_{CC} and other structure factors in such "compound forming" solutions[†].

[†] The results described in Chapters 4 and 5 are published in Bhatia and Hargrove (1973, 1974), Bhatia, Hargrove and Thornton (1974).

The concentration fluctuations S_{CC} have been recently evaluated from thermodynamic data for a number of compound forming molten alloys by several authors, notably, Ichikawa and Thompson (1973), Thompson (1974), March et. al. (1973), McAlister et. al. (1973) and Turner (1973), and Figs. 4.2-4.4 and 5.3(a-d) exhibit the variation of S_{CC} with composition for a few systems. A remarkable feature of these results is that, even for systems in which the difference in volumes of the two pure species is small (like Mg-Bi, Tl-Te, Ag-Al), S_{CC} is far from symmetric about $c = \frac{1}{2}$. This is quite in contrast to the expectation from the regular solution theory which in both and the zeroth and higher approximations predicts that G_M and hence S_{CC} be symmetric about $c = \frac{1}{2}$ (with the usual assumption that ω is independent of c).

To interpret the behaviour of S_{CC} and other structure factors in compound forming molten alloys, one has thus first to devise an appropriate expression for G_M. A first principle calculation (from statistical mechanics) of G_M is difficult for these systems and does not seem to be available. We therefore here use a phenomenological model.

It is assumed that the mixture consists of the A and B atoms and chemical associations of the type $A_\mu B_\nu$ (μ, ν small non-zero integers) in chemical equilibrium[†]. The requirement that, at constant temperature and pressure, G be a minimum then gives the equilibrium numbers of different chemical species in terms of their chemical potentials. Although a general formulation is given, the actual calculations in this chapter are carried out by making the simplifying assumption that the mixture of different chemical species can be considered as an ideal solution. For liquid (as opposed to gaseous) mixtures this assumption is admittedly approximate. However, it does make the problem considerably simpler and has been used in the past with varying degrees of semi-quantitative success to understand a variety of properties - see, for example, Bent and Hilderbrand (1927), Barfield and Schneider (1959) and Darken (1967), where other references to the literature may be found. In the next chapter we shall consider improvements upon this ideal solution assumption which will allow a more quantitative comparison with experiment.

[†] The effects of such chemical associations on S_{CC} has also been considered by McAlister and Crozier (1974) using similar methods.

The plan of the present chapter is as follows.

In §4.2, the model is described and on the basis thereof the formal expression for S_{CC} is derived. In §4.3, this is specialised by making the ideal solution assumption and is then used to discuss S_{CC} for specific cases of different μ and ν (§4.4). For comparison, S_{CC} as evaluated from measured thermodynamic data for Mg-Bi, Ag-Al and Hg-K systems are also given here. Finally, in §4.5, we apply these results to discuss the variation of partial structure factors with concentration.

4.2 Expressions for G and S_{CC}

A distinctive aspect of the molten mixtures under consideration is that in their respective solid states, they form compounds at one or more definite chemical compositions. It is therefore reasonable to assume that in the molten state of the mixture there is a strong tendency for the two types of atoms A and B to form chemical associations of the type $A_\mu B_\nu$ (where μ, ν are small non-zero integers), the precise numerical values of μ and ν depending on the mixture under consideration.

To write down a phenomenological expression for G on the above basis, consider, for definiteness,

1 gm mole of a mixture of A and B atoms, the molar fraction of A atoms being c. Let at any instant these exist as n_1 gm moles of A atoms, n_2 of B atoms and n_α gm moles of $A_{\mu_\alpha}B_{\nu_\alpha}$ molecules, where $\alpha = 3,4,....m$, and μ_α and ν_α are again small non-zero integers. From the conservation of total number of A and B atoms, we have

$$n_1 = c - \sum_{\alpha=3}^{m} \mu_\alpha n_\alpha \quad , \quad n_2 = 1 - c - \sum_{\alpha=3}^{m} \nu_\alpha n_\alpha \qquad (4.1)$$

and

$$n \equiv \sum_{i=1}^{m} n_i = 1 - \sum_{\alpha=3}^{m} (\mu_\alpha + \nu_\alpha - 1)\, n_\alpha \, . \qquad (4.2)$$

If G_i denotes the chemical potential per gm mole of the species, $i = 1,2,....m$, then the differential change in the free energy $G = \sum_i n_i G_i$ is given by (S, entropy)

$$dG = -SdT + VdP + \sum_{i=1}^{m} G_i \delta n_i \, . \qquad (4.3)$$

We can now regard n_α, $\alpha = 3,4,....m$ as order parameters whose equilibrium values are determined by the requirement that for equilibrium at constant T, P and c, G is a minimum. Hence eliminating δn_1 and δn_2 from (4.1) and setting $(\partial G/\partial n_\alpha)_{T,P,c,n_{\alpha'}} = 0$, we obtain

$$\mu_\alpha G_1 + \nu_\alpha G_2 - G_\alpha = 0 \, , \quad \alpha = 3,4,....m \, . \qquad (4.4)$$

If G_i, i = 1,2,....m, are known, Eqns. (4.4) together with (4.1) constitute m equations to determine the equilibrium values of n_1, n_2, ... n_m at a given T, P and c.

It is convenient to write the chemical potentials in the form (i = 1,2,....m)

$$G_i = G_i^{(o)} + RT\ \ell n(n_i/n) + RT\ \ell n\ \gamma_i\ , \qquad (4.5)$$

where $G_i^{(o)}$ is a function of P and T only and is just the molar Gibbs free energy for the pure species i (at the pressure and temperature of the mixture) and γ_i, by definition, is the activity coefficient of the species i. The γ_i's, in general, depend both on the various concentrations n_j/n and on P and T. If the mixture of different chemical species can be considered to form an ideal solution, then all the $\gamma_i \equiv 1$. (This assumption, of course, does not imply that the molten system considered just as a mixture of A and B atoms forms an ideal solution.) Substituting (4.5) into (4.4), one has for the equilibrium values of n_i the equations

$$\frac{(n_1\gamma_1/n)^{\mu_\alpha}(n_2\gamma_2/n)^{\nu_\alpha}}{(n_\alpha\gamma_\alpha/n)} = \exp[-\frac{g_\alpha}{RT}] \equiv K_\alpha \qquad (4.6)$$

where

$$g_\alpha = \mu_\alpha G_1^{(o)} + \nu_\alpha G_2^{(o)} - G_\alpha^{(o)}\ . \qquad (4.7)$$

and the last equality defines K_α. Under the assumption

of ideality ($\gamma_i \equiv 1$, $i = 1,2,....m$), Eqns. (4.6) become the familiar equations for studying chemical reactions, K_α being known as the reaction constants. Note that, to avoid cumbersome notation, we have denoted in (4.6) the equilibrium value of a n_i also by n_i. In the equations that follow all n_i signify equilibrium values.

The Gibbs free energy may now be written as

$$G = \sum_i n_i G_i$$

$$= cG_1^{(o)} + (1-c)G_2^{(o)} - \sum_{\alpha=3}^{m} n_\alpha g_\alpha + RT \sum_{i=1}^{m} n_i \ell n (n_i/n) + \sum_{i=1}^{m} n_i A_i \ , \tag{4.8}$$

where $A_i = RT\ \ell n\ \gamma_i$. Noting that g_α are independent of the concentration, we may then obtain by straightforward differentiations and use of (4.1), (4.2), (4.6) and the Gibbs-Duhem type of relations for A_i [†]

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,c} = cV_1^{(o)} + (1-c)V_2^{(o)} - \sum_{\alpha=3}^{m} n_\alpha v_\alpha + \sum_{i=1}^{m} n_i \left(\frac{\partial A_i}{\partial P}\right)_{T,c} \tag{4.9}$$

and

$$\frac{RT}{S_{CC}} = \left(\frac{\partial^2 G}{\partial c^2}\right)_{T,P} = RT\left(\sum_{i=1}^{m} \frac{(n_i')^2}{n_i} - \frac{(n')^2}{n}\right) + \sum_{i=1}^{m} n_i' A_i' \tag{4.10}$$

[†] These are

$$\sum_i n_i \left(\frac{\partial A_i}{\partial n_j}\right)_{T,P,n_j} = 0 \ , \quad \text{for each } j\ (= 1,2,....m) \ .$$

where $v_\alpha = (\partial g_\alpha/\partial P)_{T,c}$, and a prime denotes differentiation with respect to c. Further, $V_1^{(o)}$ and $V_2^{(o)}$ are the molar volumes of the pure liquids A and B respectively. The expressions for δ and κ_T may be obtained by differentiating (4.9) with respect to c and P, respectively.

In order to apply Eqns. (4.6)-(4.10) to a particular system, we have to specify the γ_i's and μ_α, ν_α. As already mentioned, the simplest approximation to γ_i results if one assumes that the mixture of different chemical species M_i (M_i = A, B, $A_{\mu_\alpha} B_{\nu_\alpha}$) is ideal, so that all $\gamma_i \equiv 1$. This is tantamount to assuming that there is no interaction between the different M_i. The next approximation to γ_i would then correspond to assuming pairwise interactions ω_{ij} between the different M_i which are sufficiently weak for the theory of regular solutions (in zeroth approximation) or of conformal solutions to apply. For this case γ_i are given by [Longuet-Higgins (1951)]

$$\gamma_i = \exp[A_i/RT]$$

$$= \exp\{[\sum_{j=1}^{m} (n_j/n)\omega_{ij} - \sum_{j<k}\sum (n_j/n)(n_k/n)\omega_{kj}]/RT\} \qquad (4.11)$$

with $\omega_{ij} = 0$, if $i = j$. The use of γ_i from (4.11), apart from adding a number of additional parameters (ω_{ij}), makes the problem of solving (4.6) difficult.

As mentioned earlier, we shall adopt in this chapter the ideal solution approximation ($A_i \equiv 0$, $\gamma_i \equiv 1$), with the reservation that to obtain detailed quantitative agreement more sophisticated expressions for γ_i such as (4.11) will have to be employed.

There are a number of binary alloy systems which, in the solid state, form compounds only at one stoichiometric composition, e.g. Mg-Bi at $c_{Mg} = 3/5$, Ag-Al at $c_{Ag} = 3/4$. In such cases one has to consider only one pair of values for μ, ν. The same is approximately true when the compounds are formed at more than one stoichiometric composition, provided one of these is considerably more stable than the others. For simplicity, and also since our main purpose in this chapter is to discuss broad features of the concentration fluctuations and of the partial structure factors rather than consider one specific system in detail, we shall present here results of calculation assuming that only one type of chemical associations are formed in the molten mixture.

4.3 Expressions for S_{CC} etc. for Single Pair of (μ,ν) and the Ideal Solution Assumption

It is convenient next to rewrite some of the above formulae for this simple case. We denote the single type of chemical association by $A_\mu B_\nu$ and its

molar amount by n_3. Eqns. (4.1) and (4.2) then reduce to

$$n_1 = c - \mu n_3 \quad , \quad n_2 = 1 - c - \nu n_3 \quad , \quad n = 1 - (\mu+\nu-1)n_3. \tag{4.12}$$

Further, with $\gamma_1 = \gamma_2 = \gamma_3 = 1$, Eqns. (4.5) to (4.10) yield

$$\frac{(n_1/n)^{\mu}(n_2/n)^{\nu}}{n_3/n} = \exp[-g/RT] \equiv K \ , \tag{4.13}$$

with

$$g = -RT \ \ell n \ K = \mu G_1^{(o)} + \nu G_2^{(o)} - G_3^{(o)} \ , \tag{4.14}$$

$$G = cG_1^{(o)} + (1-c)G_2^{(o)} + n_3 \ RT \ \ell n \ K + RT \sum_{i=1}^{3} n_i \ \ell n(n_i/n) \ , \tag{4.15}$$

$$V = cV_1^{(o)} + (1-c)V_2^{(o)} - n_3 v \ , \quad v = -RT(\partial \ \ell n \ K/\partial P)_T \ , \tag{4.16}$$

$$\delta = \frac{1}{V}\left(\frac{\partial V}{\partial c}\right)_{T,P,N} = \frac{V_1^{(o)} - V_2^{(o)} - n_3' v}{cV_1^{(o)} + (1-c)V_2^{(o)} - n_3 v} \ , \tag{4.17}$$

$$\theta = \frac{RT}{V^2}\left(\frac{\partial V}{\partial P}\right)_{T,c} = \frac{RT}{V^2}\left(cV_1^{(o)}\kappa_T^{(1)} + (1-c)V_2^{(o)}\kappa_T^{(2)} + \left(\frac{\partial}{\partial P}\ (n_3 v)\right)_{T,c}\right), \tag{4.18}$$

and

$$S_{CC} = \left(\sum_{i=1}^{3} \frac{(n_i')^2}{n_i} - \frac{(n')^2}{n}\right)^{-1} \ . \tag{4.19}$$

From (4.12)

$$n_1' = 1 - \mu n_3' \ , \quad n_2' = -1 - \nu n_3' \ , \quad n' = -(\mu + \nu - 1)\, n_3' \ . \tag{4.20}$$

Hence remembering that K is independent of concentration, we have from (4.13)

$$n_3' = \frac{[(\mu + \nu)c - \mu]\, n\, n_3}{n_1 n_2 n_3 (\mu+\nu-1)^2 - \mu^2 n\, n_2 n_3 - \nu^2\, n\, n_1 n_3 - n n_1 n_2} \quad . \quad (4.21)$$

Care must be taken in using (4.21) at c = 0 and c = 1, since here n_3 and one of n_1 and n_2 simultaneously tend to zero.

Finally in evaluating θ one needs $(\partial n_3/\partial P)_{T,c}$, which is given by, from (4.12) and (4.13),

$$\left(\frac{\partial n_3}{\partial P}\right)_{T,c} = \frac{v}{RT}\left(\frac{\mu^2}{n_1} + \frac{\nu^2}{n_2} + \frac{1}{n_3} - \frac{(\mu + \nu - 1)^2}{n}\right)^{-1} \quad . \quad (4.22)$$

We observe from the above equations that the determination of concentration fluctuations (S_{CC}) requires only the knowledge of the reaction constant K. An approximate value of K for a specific system may be inferred from (4.15) and the experimental data on the free energy of mixing $G_M = G - cG_1^{(o)} - (1-c)G_2^{(o)}$. The determination of V and θ from Eqns. (4.16) and (4.18) requires the knowledge of v and $(\partial v/\partial P)_T$ respectively, which are related to the first and second derivatives of K with respect to pressure. In practice v may be inferred from the data on volume. θ is usually small (∿0.03) and may, in the absence of experimental data and to a first approximation, be linearly interpolated between its values for the two pure liquids.

4.4 Concentration Fluctuations S_{CC} for Different μ,ν

We now use Eqns. (4.13) and (4.19) to calculate the concentration fluctuations S_{CC} as a function of concentration and the reaction constant K for different pairs of values of μ and ν.

4.4.1 Limiting Cases

If we eliminate n_1 and n_2, using (4.12), Eqn. (4.13) becomes an algebraic equation of degree $\mu+\nu$ in n_3. Hence, except for the case $\mu = 1$ and $\nu = 1$, one has to solve (4.13) numerically and then obtain S_{CC}. Before presenting the numerical results it will be useful first to consider certain limiting cases.

a) $K \to \infty$

First, if $K = \infty$, one can readily see from (4.13) that $n_3 = 0$ and also $(n_3')^2/n_3 = 0$. Then $n_1 = c$, $n_2 = 1-c$, and one has from (4.19) and (4.20)

$$S_{CC}^{id} = c(1-c) , \qquad (4.23)$$

where, as before, the superscript id on S_{CC} indicates that the binary mixture behaves like an ideal solution in this case.

b) $K \to 0$

The solutions in which molecular formations occur to a marked degree form the opposite case. Here

$K \ll 1$, with typical values of $10^{-1} - 10^{-4}$. We therefore consider the limiting case $K = 0$, although physically K can never be zero as it corresponds to infinitely large negative free energy of mixing (cf. Eqn. (4.15)). We shall see presently that the simple expression for S_{CC} for $K = 0$ corresponds closely to the S_{CC} for a non-zero $K \ll 1$.

With $K = 0$, (4.13) implies that either $n_1 = 0$, so that $n_3 = c/\mu$, or $n_2 = 0$ so that $n_3 = (1-c)/\nu$. Remembering that the maximum possible value of n_3 is $n_3 = (\mu+\nu)^{-1}$, we have

$$n_3 = c/\mu \qquad \text{for} \quad 0 < c \leq \mu/(\mu+\nu) \quad , \qquad (4.24)$$

$$n_3 = (1-c)/\nu \quad \text{for} \quad \mu/(\mu+\nu) \leq c < 1 \quad . \qquad (4.25)$$

The concentrations $c = 0$ and $c = 1$ are excluded from the ranges of c in (4.24) and (4.25). Here $n_3 = 0$ so that the left hand side of Eqn. (4.13) has the form 0/0 and it needs special consideration to which we come presently.

When (4.24) is valid, one has

$$n_1 = 0 \quad , \quad n_2 = 1 - c - c\nu/\mu \quad , \quad n = 1 - (\mu+\nu-1)c/\mu \qquad (4.26)$$

and $(n_1')^2/n_1 = 0$.

Hence using (4.19) and (4.20) one obtains

$$S_{CC} = \frac{c}{\mu}\,[\mu - c(\mu+\nu)][\mu - (\mu+\nu-1)c] \quad , \quad 0 < c \leq \frac{\mu}{\mu+\nu} \quad . \qquad (4.27)$$

Similarly when (4.25) is valid

$$S_{CC} = \frac{(1-c)}{\nu}[\nu-(1-c)(\mu+\nu)][\nu-(1-c)(\mu+\nu-1)], \quad \frac{\mu}{\mu+\nu} \leq c < 1 . \tag{4.28}$$

Note that (4.28) may be obtained from (4.27) by replacing everywhere in (4.27) c by 1-c, μ by ν and ν by μ. Since (4.27) is, in general, not valid at c = 0, it cannot be used to calculate the slope of S_{CC} at c = 0, and, in fact, gives incorrectly this slope except when $\mu = 1$ (see Eqns. (4.38)-(4.40) below). Similar remarks apply to (4.28) at c = 1.

c) <u>$c \ll 1$, $K \ll 1$</u>

To obtain S_{CC} and its slope near c = 0 and c = 1, let us go back to Eqn. (4.13) with $K \neq 0$ and rewrite it in the form, using (4.12),

$$(c - \mu n_3)^{\mu}(1 - c - \nu n_3)^{\nu} = K n_3[1 - (\mu+\nu-1)n_3]^{\mu+\nu-1} . \tag{4.29}$$

Consider first the case $c \ll 1$. Then noting that n_3 is necessarily less than or equal to c/μ, we have, to leading order in small quantities,

$$(c - \mu n_3)^{\mu} \approx K n_3$$

or

$$y^{\mu} + K'y - c = 0 , \tag{4.30}$$

where

$$y = (\mu n_3)^{1/\mu} , \quad K' = (K/\mu)^{1/\mu} . \tag{4.31}$$

For $\mu = 1$, (4.30) gives

$$y = n_3 \simeq c/(1+K) , \quad \text{for} \quad \mu = 1 . \tag{4.32}$$

For $\mu \geq 2$, we can neglect, for sufficiently small c, the first term in (4.30) compared to the second term and hence

$$y \simeq c/K' \quad \text{or} \quad n_3 \simeq c^{\mu}/K , \quad \mu \geq 2 . \tag{4.33}$$

(4.33) is clearly valid if $(c/K')^{\mu} << c$, or

$$c << (K/\mu)^{1/(\mu-1)} . \tag{4.34}$$

Noting that (4.32) and (4.33) are correct to the power of c exhibited in them, and using Eqns. (4.12), we can readily expand the expression (4.19) for $(S_{CC})^{-1}$ in powers of c. One finds, for $\mu = 1$,

$$S_{CC}^{-1} = c^{-1} + 1 + 2\nu/(1+K) + O(c) , \quad \mu = 1 \tag{4.35}$$

and for $\mu \geq 2$

$$S_{CC}^{-1} = c^{-1} + 1 - K^{-1} \mu(\mu-1)c^{\mu-2} + O(c^{\mu-1}) . \tag{4.36}$$

For comparison

$$(S_{CC}^{id})^{-1} = c^{-1} + 1 + c + c^2 + \ldots\ldots . \tag{4.37}$$

From (4.35) and (4.36), we have, to order c^2,

$$S_{CC} = c - c^2 - \frac{2\nu}{1+K} c^2 + O(c^3) , \quad \mu = 1 , \qquad (4.38)$$

$$S_{CC} = c - c^2 + (2/K)c^2 + O(c^3), \quad \mu = 2 , \qquad (4.39)$$

$$S_{CC} = c - c^2 + O(c^3) , \quad \mu \geq 3 . \qquad (4.40)$$

The expressions for S_{CC}^{-1} and S_{CC} near c = 1 are simply obtained from Eqns. (4.35)-(4.40) by replacing everywhere c by 1-c, μ by ν and ν by μ.

4.4.2 Discussion and Numerical Results

Eqns. (4.35)-(4.40) show firstly that in every case as $c \to 0$, $S_{CC} \to c$, as it should. Secondly, as c increases from zero (but still $c \ll 1$), S_{CC} increases and lies below the ideal value if $\mu = 1$ and above it if $\mu \geq 2$. With further increase of c, Eqn. (4.27) shows that S_{CC} has a maximum at some concentration, say, $\tilde{c}_1$ ($\tilde{c}_1 < \mu/\mu+\nu$), and then drops to zero at $c = \mu/\mu+\nu$. S_{CC} has a discontinuous slope at this point, since as c increases further Eqn. (4.28) takes over and S_{CC} rises again to a maximum, at the concentration, $\tilde{c}_2$, say, and then decreases to zero, the limiting behaviour near c = 1 being governed by whether $\nu = 1$ or $\nu \geq 2$ in accordance with equations similar to (4.35)-(4.40).

It is interesting to remark here that the fact that (for $K \to 0$), $S_{CC} = 0$ at $c = \mu/\mu+\nu$ and has a V-shaped variation with concentration near $c = \mu/\mu+\nu$ is similar

to the behaviour of the concentration fluctuations in a perfectly ordered solid alloy near the appropriate stoichiometric composition [Krishnan and Bhatia (1944), Bhatia and Thornton (1970)]. For the latter at the stoichiometric composition itself, of course, $S_{CC}(\underset{\sim}{q}) = 0$ for all wave vectors $\underset{\sim}{q}$ except for the spikes which correspond to Bragg reflections due to the formation of the superlattice. In a compound forming molten solution at the chemical composition, $S_{CC}(q)$ may then be expected to be much smaller than S_{CC}^{id} for small q, have a peak higher than S_{CC}^{id} at some higher q and then oscillate about S_{CC}^{id} with progressively damped amplitude with the sum rule for $S_{CC}(q)$ given by Eqn. (2.21b).

Returning to Eqns. (4.27)-(4.28), we may deduce from them that the positions $\tilde{c}_1$ and $\tilde{c}_2$ of the two maxima in S_{CC} and their heights are given by

$$\tilde{c}_1 = (\mu/y)f(y) \quad , \qquad \tilde{c}_2 = 1 - (\nu/y)f(y) \quad , \tag{4.41}$$

$$S_{CC}(\tilde{c}_1) = (\mu/y)^2 f(y)(1-f(y))[y+f(y)(1-y)], \tag{4.42}$$

$$S_{CC}(\tilde{c}_2) = (\nu/\mu)^2 S_{CC}(\tilde{c}_1) \quad , \tag{4.43}$$

where $y = \mu+\nu$ and

$$f(y) = \frac{2y - 1 - (y^2 - y + 1)^{\frac{1}{2}}}{3(y-1)} \quad . \tag{4.44}$$

We note that the heights of the two peaks are in general

unequal being in the ratio $(\mu/\nu)^2$. Table 4.1 gives values of $\tilde{c}_1$, $\tilde{c}_2$ and the heights of the peaks for some values of μ and ν.

For a non-zero K, but $K \ll 1$ the positions and heights of the peaks would still be roughly given by Eqns. (4.41)-(4.42), while the V-shaped behaviour near $c = \mu/\mu+\nu$ will get rounded into a minimum. With further increase in K, the two maxima will gradually merge into each other in accordance with the limiting behaviour $S_{CC}^{id} = c(1-c)$ for $K \to \infty$. These features are illustrated in Figs. 4.1-4.4, where we give the results of numerical calculations for S_{CC} for different values of K for the cases $(\mu,\nu) = (1,1)$, $(3,2)$, $(3,1)$ and $(2,1)$.

In Fig. 4.2, we also give the experimental values of S_{CC} for Mg-Bi system which is known to form the compound Mg_3Bi_2 in the solid state. These were obtained from the data on the activities tabulated in Hultgren et. al. (1963), by noting that if γ_A is the activity coefficient of metal A (concentration c) in the binary solution, then†

---

† Eqn. (4.45) follows immediately from (2.41) if we note that the activities a_1 and a_2 in it are related to γ_A and γ_B by $a_1 (\equiv a_A) = c\,\gamma_A$ and $a_2 (\equiv a_B) = (1-c)\gamma_B$. We mention that, in certain ranges of concentration, a precise determination of the slopes of $\ell n\, a$ or $\ell n\, \gamma$ versus c curves (and hence S_{CC}) requires more data than is presently available.

Table 4.1

The positions ($\tilde{c}_1$ and $\tilde{c}_2$) and heights of the peaks in S_{CC} for the limiting case $K \to 0$ for some pairs of μ,ν. For comparison the value of $S_{CC}^{id} = c(1-c)$ at each of the concentration is also given.

$\mu+\nu$	μ	ν	$\tilde{c}_1$	$S_{CC}(\tilde{c}_1)$	$S_{CC}^{id}(\tilde{c}_1)$	$\tilde{c}_2$	$S_{CC}(\tilde{c}_2)$	$S_{CC}^{id}(\tilde{c}_2)$
2	1	1	0.212	0.096	0.167	0.788	0.096	0.167
3	2	1	0.261	0.232	0.193	0.87	0.058	0.113
4	3	1	0.283	0.379	0.203	0.906	0.042	0.085
5	4	1	0.294	0.52	0.208	0.926	0.033	0.069
9	8	1	0.310	1.111	0.214	0.96	0.0174	0.038
5	3	2	0.221	0.295	0.172	0.853	0.131	0.125

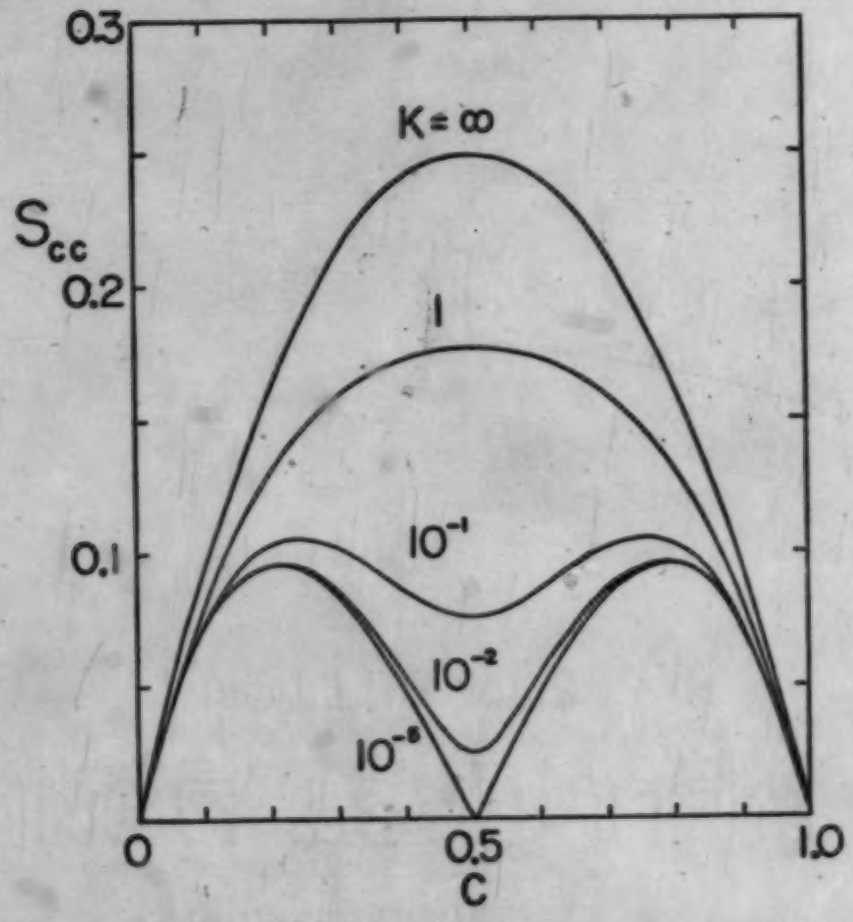

Fig. 4.1. The concentration fluctuations S_{CC} as a function of concentration in a binary mixture forming chemical associations of the AB type ($\mu=\nu=1$). The different curves are for different values of the reaction constant K as marked; the curve $K=\infty$ represents $S_{CC} = S_{CC}^{id} = c(1-c)$.

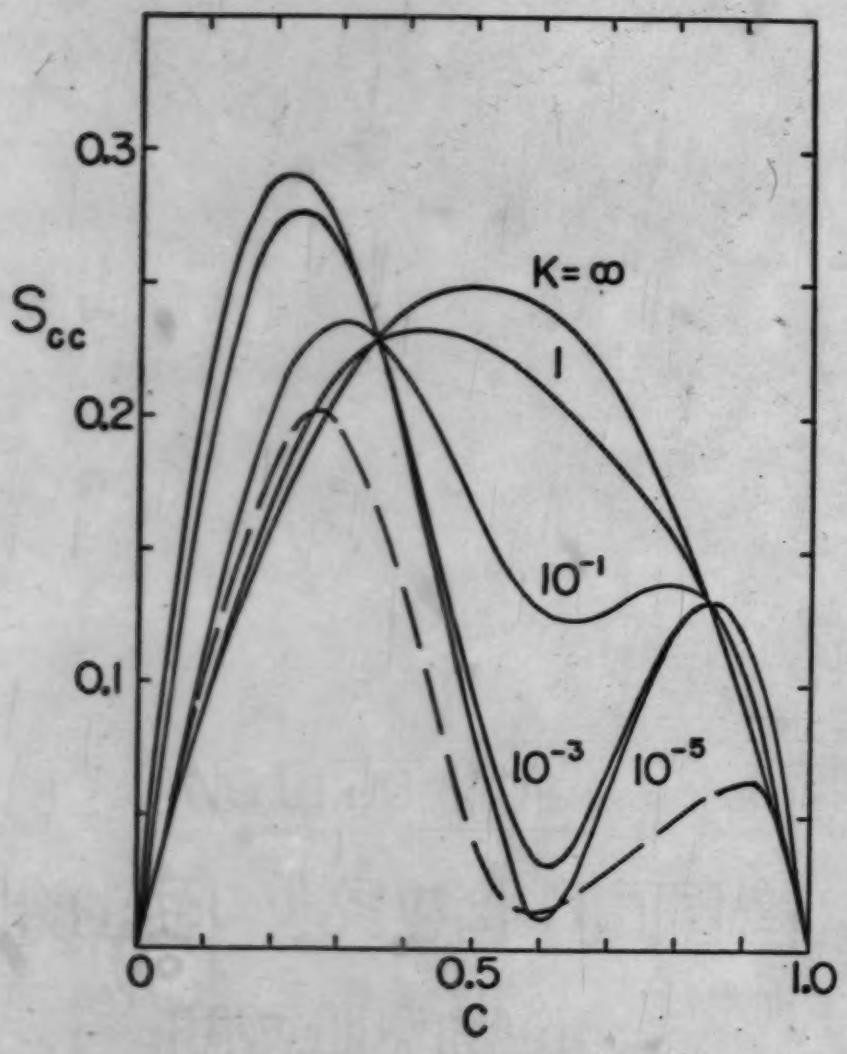

Fig. 4.2. S_{CC} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the A_3B_2 type (μ=3, ν=2). —, theoretical for different values of the reaction constant K; — —, experimental from data of Hultgren et.al. (1963) [see also Ichikawa and Thompson (1973)] for the Mg-Bi system with $c = c_{Mg}$.

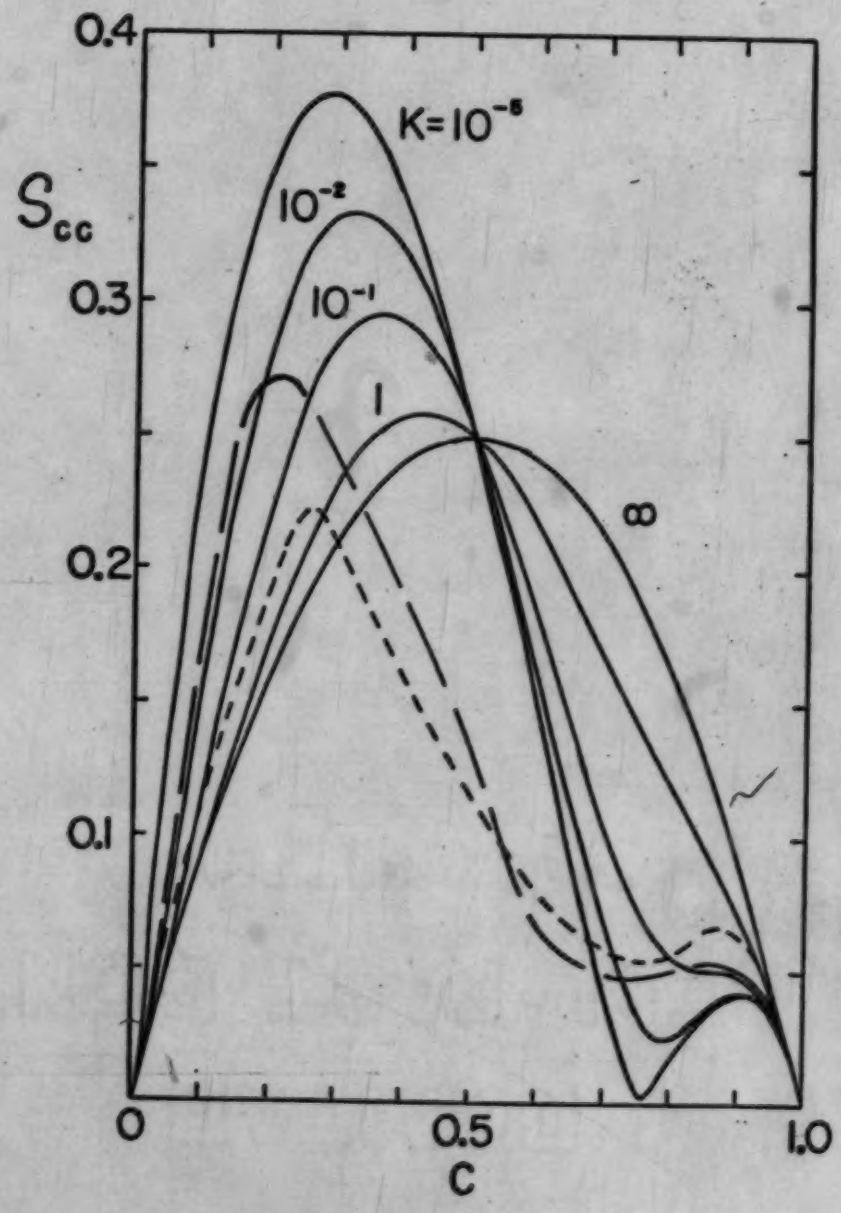

Fig. 4.3. S_{CC} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the A_3B_1 type ($\mu=3$, $\nu=1$). —, theoretical for different values of the reaction constant K; — —, experimental from data of Hultgren et.al. (1963) for the Ag-Al system; ---, experimental from data of Wilder and Elliot (1960) for the Ag-Al system with $c = c_{Ag}$.

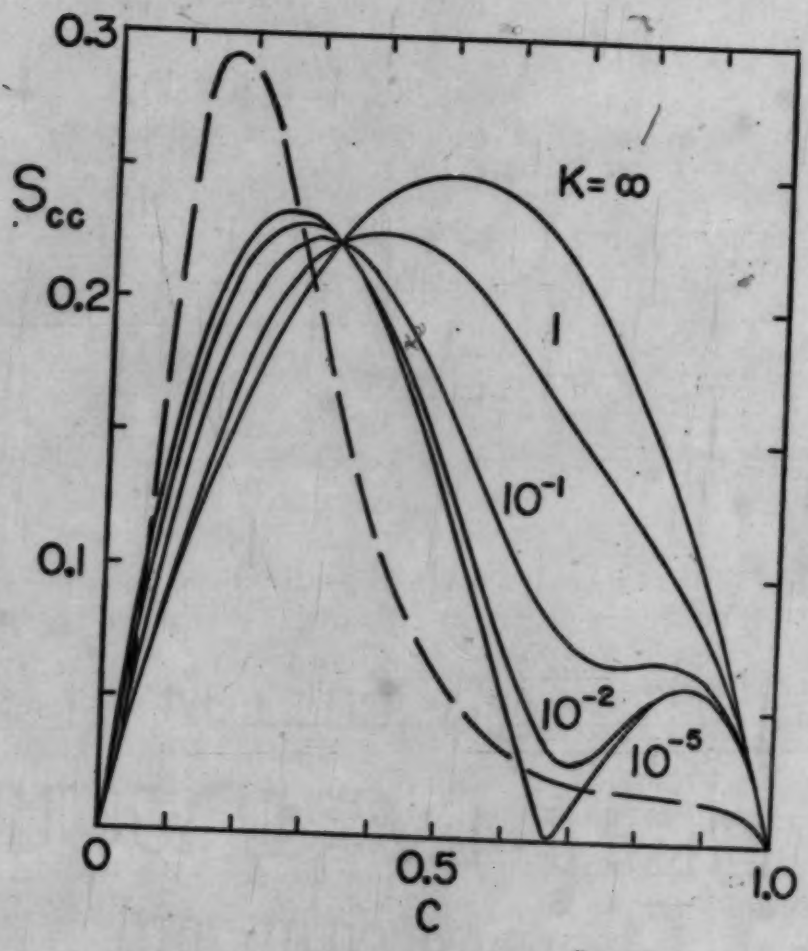

Fig. 4.4. S_{CC} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the A_2B_1 type (μ=2, ν=1). —, theoretical for different values of the reaction constant K; — —, experimental from data of Hultgren et.al. (1963) for the Hg-K system with $c = c_{Hg}$.

$$S_{CC} = \frac{c(1-c)}{1+c\left(\frac{\partial \ln \gamma_A}{\partial c}\right)_{T,P}} = \frac{c(1-c)}{1-(1-c)\left(\frac{\partial \ln \gamma_B}{\partial c}\right)_{T,P}} \quad . \qquad (4.45)$$

The data on free energy of mixing for this alloy at the temperature concerned suggests that $K \sim 10^{-6} - 10^{-4}$. We see that the experimental S_{CC} has a minimum and two maxima at approximately the right concentrations and their heights are of the right orders of magnitude.

Fig. 4.3 similarly shows the experimental values of S_{CC} for the Ag-Al system, which in the solid state forms the compound Ag_3Al. These were obtained from the data given by Hultgren et. al. (1963) and also that given by Wilder and Elliott (1960). For this system the free energy data suggests $K \sim 10^{-2}$ and we see that the minimum at $c_{Ag} \simeq \frac{3}{4}$ is very shallow compared to that in the Mg-Bi system at $c_{Mg} = \frac{3}{5}$, as expected.

Finally, in Fig. 4.4 ($\mu = 2$, $\nu = 1$), the experimental values of S_{CC} for the Hg-K system are given. Here $K \sim 10^{-5} - 10^{-4}$. We see that the height and the position of the first peak, and the low values of S_{CC} near $c_{Hg} \simeq \frac{2}{3}$ are fairly well reproduced by the theoretical curves, but the experimental curve shows no second maximum. The experimental S_{CC} for Hg-Na is similar for $c_{Hg} \lesssim \frac{1}{2}$, but the height of the first peak is substantially less than that for the Hg-K system. These

discrepancies are probably at least partly due to the fact that these solutions, in the solid state, form not only the compound Hg_2B ($B \equiv$ K or Na) but also HgB, Hg_4B and Hg_8B, so that several pairs of (μ,ν) should be simultaneously taken into consideration (see Eqn. (4.10)).

Finally, as a contrast to the behaviour of S_{CC} depicted in Figs. 4.1-4.4, we may recall the variation of S_{CC} with concentration for the regular (in the zeroth approximation)† or conformal solutions. For these S_{CC} is given by (3.34), namely,

$$S_{CC} = \frac{c(1-c)}{1 - \frac{2\omega}{RT} c(1-c)} \qquad (4.46)$$

so that it is symmetric about $c = \frac{1}{2}$, has a maximum at $c = \frac{1}{2}$ and lies, for all c, either above $S_{CC}^{id} = c(1-c)$ or below S_{CC}^{id}, depending upon whether the interchange energy ω is positive or negative.

---

† Parenthetically we mention that, as might be expected, the regular solution theory in the higher (quasi-chemical, see §3.4) approximation, gives for S_{CC} essentially the same results as depicted in Fig. 4.1 - which is for the case $\mu = \nu = 1$ and hence is symmetric about $c = \frac{1}{2}$.

From the above discussion, it is apparent that the simplified version of the model (on which the calculations are presented here) has reasonable applicability to at least some of the compound forming solutions, although in general other factors (more than one type of $A_\mu B_\nu$ and deviation from the assumption of ideality, see Eqn. (4.10)) have to be considered for obtaining quantitative agreement.

4.5 Variation of Partial Structure Factors with Concentration

Knowing S_{CC}, it is relatively a simple matter to infer the concentration dependence of the partial structure factors a_{ij} or of the other two number-concentration structure factors S_{NN} and S_{NC} (see §3.2).

For this purpose we require θ and δ. Of these, as mentioned earlier, θ is usually small ($\sim$0.03) and in the absence of experimental data may, to a first approximation, be assumed to vary linearly with c between the two pure metals. δ may be inferred from the data on volume as a function of concentration, which, if the simplified version of the model is valid, should be given by (4.16), in which we need only to fix the parameter v (and, of course, $V_1^{(o)}$ and $V_2^{(o)}$) from the observed data. In this connection we should note that according to (4.16), the excess volume ΔV, i.e. the

actual volume of the mixture minus the volume obtained by linear interpolation between the values for the two pure liquids, is given by

$$\Delta V = V - cV_1^{(o)} - (1-c)V_2^{(o)} = -n_3 v \ . \qquad (4.47)$$

Hence $|\Delta V|$ is maximum when n_3 is maximum, that is at the concentration $c = \mu/\mu+\nu$. For many cases $\Delta V/V$ is at most a few percent and we have not been able to verify this conclusion for lack of sufficient data. (In these cases, δ calculated by assuming the linear dependence of volume on c forms a reasonable approximation, cf. Fig. 3.8). For the amalgams discussed earlier, HgK and HgNa, the observed maximum in $|\Delta V|$ ($\sim$0.24V and 0.18V respectively) occurs near $c = \frac{1}{2}$ [Degenkolbe and Sauerwald (1952), Vanstone (1911)]. We have already mentioned the reasons why the simplified version of the model taking $\mu = 2$ and $\nu = 1$ is not quite adequate for these systems.

When the tendency to form chemical associations $A_\mu B_\nu$ is strong ($K << 1$), the variation of a_{ij} with concentration depends markedly on the values of μ and ν. To illustrate this feature and to see how this variation is affected by δ, we depict a_{ij} versus concentration curves for a few cases in Figs. 4.5-4.7. For simplicity we have throughout set $\theta = 0$ and drawn all the curves for $K = 10^{-3}$. As will be clear from the inspection of Figs. 4.1-4.4 for S_{CC}, a smaller value of K

does not affect the results qualitatively. (For $K \to \infty$, $S_{CC} \to S_{CC}^{id}$ $(=c(1-c))$, and the concentration dependence of a_{ij} is quite different from that depicted in these figures; for example, if $\delta = 0$, then all $a_{ij} = \theta \sim 0.03$, and if $\beta = 2$ or $\frac{1}{2}$ a_{ij} are as given in Figs. 3.2-3.3.

Fig. 4.5 gives the results for the cases $(\mu,\nu) = (1,1)$ and $(3,1)$ taking $\delta = 0$ (equal partial molar volumes for the two species at all c). The curves for $(\mu,\nu) = (1,1)$ are qualitatively similar to those given in Faber (1972). The dashed curves in Fig. 4.6 show the concentration dependence of a_{ij} for $\mu = 3$, $\nu = 2$ case taking $\delta = 0$, while the smooth curves are drawn by assuming that the volume varies linearly between the volumes of the two pure constituents. The numerical values for the volumes were chosen appropriate to the Mg-Bi system, so that $\delta(c)$ varies monotonically with concentration from -0.29 at c = 0 to -0.4 at c = 1. These values of $\delta(c)$ should be correct to about 10% for this system since $\Delta V \simeq 0.02$ V at the composition Mg_3Bi_2.

Lastly, Fig. 4.7 gives the results for $\mu = 2$, $\nu = 1$ case. The curves with long dashes are again for $\delta = 0$, while the smooth curves are drawn using $\delta(c)$ obtained from the measured data on volumes for the K-Hg system [Dagenkolbe and Sauerwald (1952)]. ($\delta(c)$ first decreases from $\delta(0) \simeq -1.3$ to $\delta(\frac{1}{2}) = -1.5$ and then

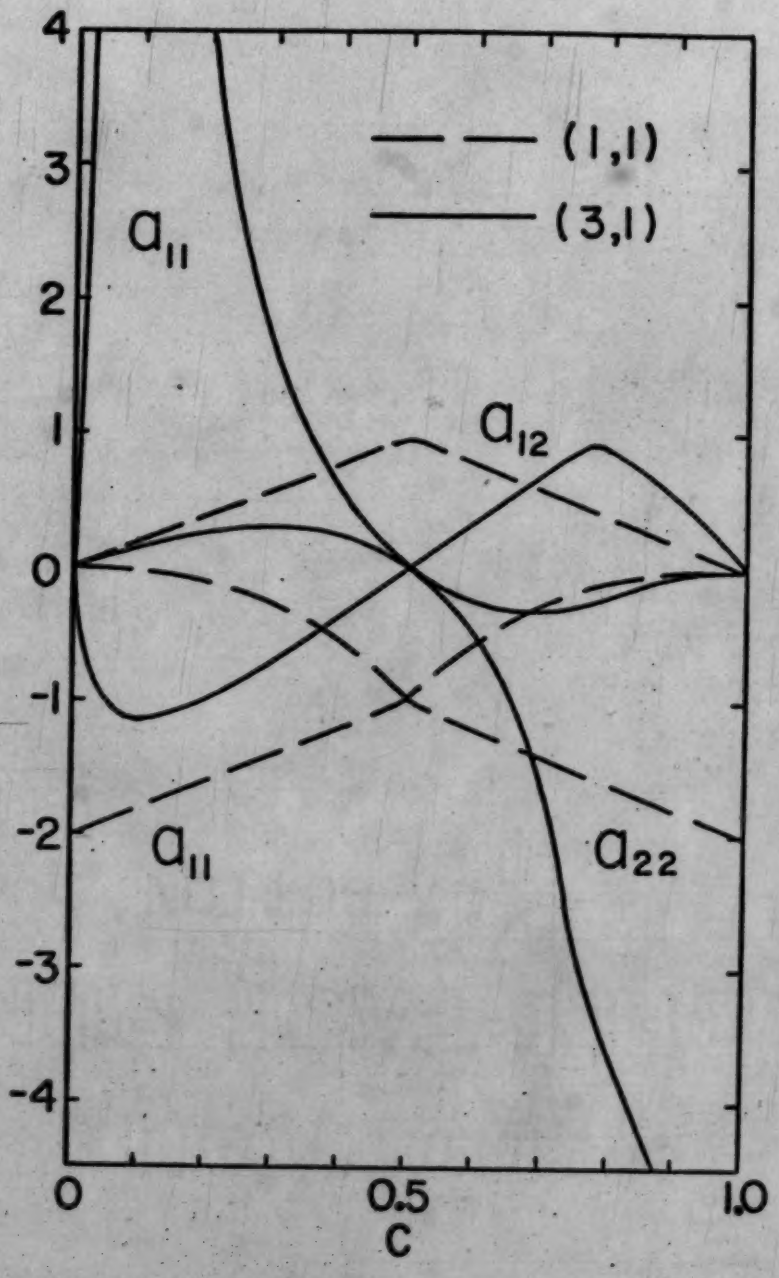

Fig. 4.5. The partial structure factors a_{ij} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the $A_\mu B_\nu$ type. — —, $\mu = \nu = 1$; —, $\mu = 3, \nu = 1$. Both sets of curves are for $\delta = 0$ (equal partial molar volumes for the two species).

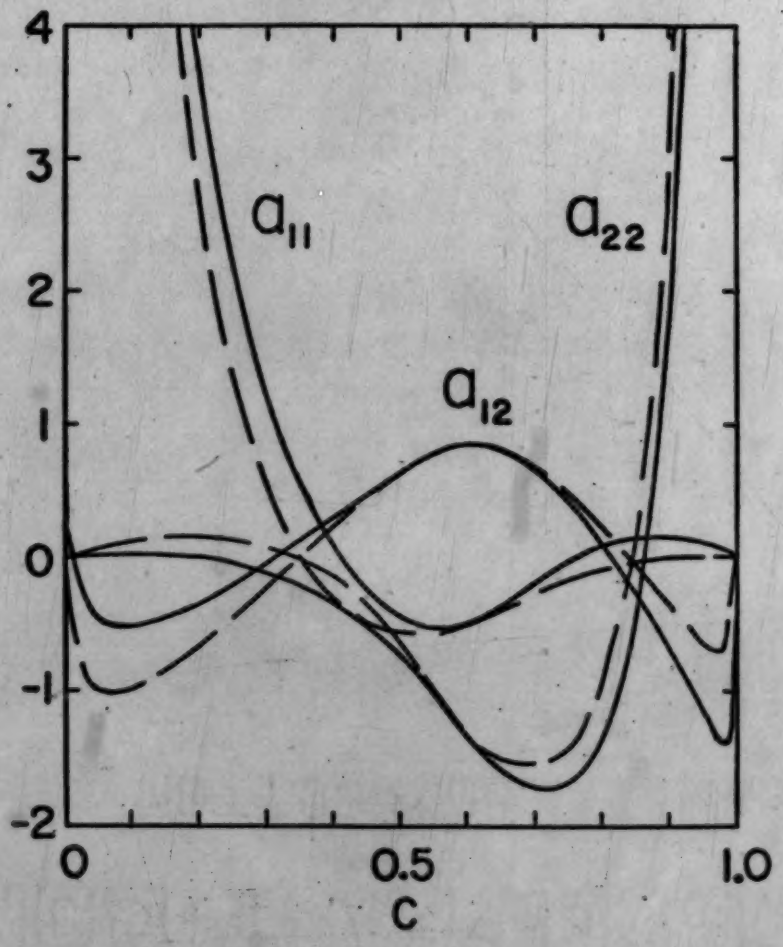

Fig. 4.6. The partial structure factors a_{ij} as a function of concentration c of $\bar{A}$ atoms in a binary mixture forming chemical associations of the type A_3B_2 ($\mu=3, \nu=2$). — —, $\delta=0$; —, δ, as explained in the text. For values of a_{11} near $c=0$ and of a_{22} near $c=1$, not shown in the diagram, see text following eqn. (4.56).

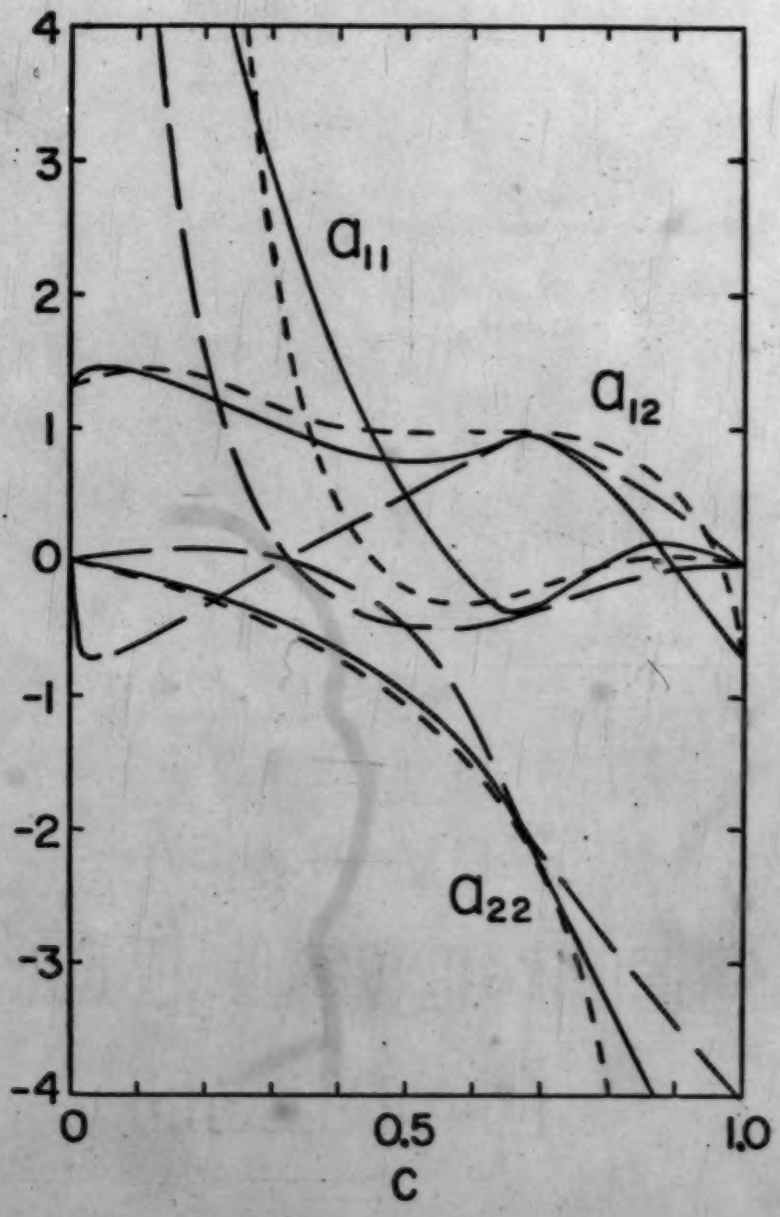

Fig. 4.7. The partial structure factors a_{ij} as a function of concentration c of A atoms in a binary mixture forming chemical associations of the type A_2B_1 ($\mu=2,\nu=1$). — —, theoretical with $\delta = 0$; —, theoretical with δ as explained in the text; ---, experimental from McAlister and Turner (1972) for the Hg-K system with $c = c_{Hg}$.

increases monotonically to $\delta(1) \simeq -0.7$). For comparison the values of a_{ij} obtained by McAllister and Turner (1972) from the measured thermodynamic data are also given. Considering the limitations of the model discussed earlier and the uncertainty in determining S_{CC} from the measured activity data, the agreement between the two is not unsatisfactory.

The results presented above need two further comments. First, we observe that in Figs. 4.6 and 4.7 the dashed ($\delta = 0$) and smooth ($\delta \neq 0$) curves for each a_{ij} come very close to each other near the appropriate chemical composition. This is not surprising if we refer to Eqn. (2.36) for a_{ij} and consider the limiting case $K \to 0$. Then since now $S_{CC} = 0$ at the stoichiometric composition $c(\equiv c_1) = \mu/\mu+\nu$, the partial structure factors become independent of δ at this composition, and are given by (with $\theta = 0$)

$$a_{11} = -\frac{\nu}{\mu}, \quad a_{22} = -\frac{\mu}{\nu} \quad \text{and} \quad a_{12} = +1, \quad \left(c = \frac{\mu}{\mu+\nu}\right). \qquad (4.48)$$

The values of a_{ij} for $K = 10^{-3}$ given in Figs. 4.6 and 4.7 are close to these values at $c = \frac{3}{5}$ and $c = \frac{2}{3}$ respectively.

Second, it is of interest to give explicit expressions for the values of $a_{ij}(c)$ at $c = 0$ and $c = 1$. If we substitute the expansions (4.38)-(4.40) for S_{CC} into the Eqn. (2.36) and take the limit $c \to 0$ (or $c \to 1$

as the case may be), we obtain ($a_{ij}(c=0) \equiv a^{o}_{ij}$ etc.)

$$a^{1}_{11} = \theta^{1} \quad , \quad a^{o}_{22} = \theta^{o} \qquad \text{for all } \mu \text{ and } \nu, \qquad (4.49)$$

$$a^{o}_{12} = \theta^{o} - \delta^{o}, \; a^{1}_{12} = \theta^{1} + \delta^{1} \qquad \text{for all } \mu \text{ and } \nu, \qquad (4.50)$$

$$a^{o}_{11} = \theta^{o} - 2\delta^{o} - 2\nu(1+K)^{-1} \quad , \quad \text{for } \mu = 1 \quad , \qquad (4.51)$$

$$= \theta^{o} - 2\delta^{o} + 2/K \quad , \quad \text{for } \mu = 2 \quad , \qquad (4.52)$$

$$= \theta^{o} - 2\delta^{o} \quad , \quad \text{for } \mu \geq 3 \quad , \qquad (4.53)$$

and

$$a^{1}_{22} = \theta^{1} + 2\delta^{1} - 2\mu(1+K)^{-1}, \quad \text{for } \nu = 1 \quad , \qquad (4.54)$$

$$= \theta^{1} + 2\delta^{1} + 2/K \quad , \quad \text{for } \nu = 2 \quad , \qquad (4.55)$$

$$= \theta^{1} + 2\delta^{1} \quad , \quad \text{for } \nu \geq 3 \quad . \qquad (4.56)$$

Thus, for example, in Fig. 4.6 ($\mu = 3$, $\nu = 2$), the dashed curve for a_{11} starts from zero and steeply rises with small increase in the concentration, has a large maximum ($\sim$33, not shown in the diagram) at $c \simeq 0.01$, and then follows the curve as in the diagram. In contrast a_{22}, near $c = 1$, continues to rise to the value $a^{1}_{22} \simeq 2K \simeq 2000$ in accordance with (4.55). As shown by Eqns. (3.10) and (3.11), a^{o}_{11} and a^{1}_{22} depend on the curvature of S_{CC}, i.e. d^2S_{CC}/dc^2, at $c = 0$ and $c = 1$ respectively, so that their determination from experimental S_{CC} is difficult. The limits given in Eqns. (4.51) to (4.56) may therefore serve as useful guidelines where the model is applicable.

CHAPTER 5

CONCENTRATION FLUCTUATIONS AND THERMODYNAMIC PROPERTIES OF SOME COMPOUND FORMING BINARY MOLTEN SYSTEMS

5.1 Introduction

In the previous chapter we discussed some general characteristics of the concentration fluctuations S_{CC} and other structure factors in the compound forming binary molten systems on the basis of the so-called chemical approach. This assumes that if the mixture of A and B atoms forms, in the solid state, a compound at a single chemical composition† specified by $A_\mu B_\nu$ (μ , ν small integers), then in the liquid state there exist, at a given temperature and pressure, certain numbers of A and B atoms and chemical complexes $A_\mu B_\nu$ in chemical equilibrium with one another. The equilibrium numbers of these and hence the macroscopic thermodynamic properties of the binary mixture depend on (a) the (free)

---

† The more general case where compounds are formed at more than one chemical composition was also formulated in the chapter, but will not be pursued here. If one of the compounds is considerably more stable (for example, has much higher melting point) than the others, one may as a first approximation assume that one type of chemical complexes is formed.

energy of formation of the chemical complexes or the reaction constant, and on (b) the form of the chemical potentials assumed for A,B and $A_\mu B_\nu$, that is, whether the ternary mixture can be regarded to behave like an ideal, athermal, conformal solution etc.

The behaviour of S_{CC} etc. for different values of μ and ν was discussed in Chapter 4 by making the simplest, namely, the ideal solution assumption referred to in (b) above. However, this assumption is too crude to give, in general, quantitative agreement with experiment. In this chapter we discuss two higher approximations and calculate on their bases the concentration dependence of the free energy of mixing, the activity and S_{CC} for four binary systems: Tl-Te, Mg-Bi, Cu-Sn and Ag-Al. Each of these higher approximations contains four interaction parameters, and although these have physical interpretation they have to be at present determined from the thermodynamic data themselves.

The two approximations are described in §5.2 and the various relevant formulae are derived on the bases thereof in §5.3. In §5.4 the behaviour of S_{CC} is discussed for two limiting cases for which the equilibrium equation can be solved analytically. The results of numerical calculations and comparison with experiment are presented in §5.5. This is followed by a brief discussion of the results and some concluding remarks.

5.2 Basic Formulae and Approximations

Let the binary solution contain in all $N_A = \mathcal{N}c$ and $N_B = \mathcal{N}(1-c)$ gm moles of A and B atoms respectively, c being the atomic fraction of A atoms. We assume that only one type of chemical complexes $A_\mu B_\nu$ (μ,ν small integers) are formed. Then if there are in the solution n_1 gm moles of A atoms, n_2 of B atoms and n_3 gm moles of $A_\mu B_\nu$, we have from conservation of atoms

$$n_1 = \mathcal{N}c - \mu n_3 , \qquad n_2 = \mathcal{N}(1-c) - \nu n_3$$

and

$$n = n_1 + n_2 + n_3 = \mathcal{N} - (\mu+\nu-1)n_3 . \tag{5.1}$$

The free energy of mixing for the binary A-B alloy can obviously be written as

$$G_M = G - \mathcal{N}cG_1^{(o)} - \mathcal{N}(1-c)G_2^{(o)}$$

$$= - n_3 g + G' \tag{5.2}$$

with

$$g = \mu G_1^{(o)} + \nu G_2^{(o)} - G_3^{(o)} \tag{5.3}$$

$$G' = G - (n_1 G_1^{(o)} + n_2 G_2^{(o)} + n_3 G_3^{(o)}) , \tag{5.4}$$

where $G_i^{(o)}$, i = 1,2,3, is the chemical potential for the pure species i in the solution. The equilibrium value of n_3 at a given concentration, pressure and temperature is given by the condition that G and hence

G_M be a minimum, i.e.

$$(\partial G_M/\partial n_3)_{T,P,\mathcal{N},c} = 0 \ . \qquad (5.5)$$

We remark that in Chapter 4 we had formulated the problem somewhat differently (using the language of chemistry rather than physics!). The equivalence of the two formulations is demonstrated and their relative convenience commented upon in Appendix 1.

In (5.2), the first term $(-n_3 g)$ represents the lowering of the (free) energy due to the formation of the chemical complexes. The second term is the free energy of mixing of a ternary mixture of fixed n_1, n_2, n_3, whose constituents A,B and $A_\mu B_\nu$ will be assumed to interact relatively weakly with one another - the strong bonding interaction between A and B atoms having been already taken care of via the formation of chemical complexes. We may thus borrow expressions of varying complexity for G' from the various theories of weakly interacting mixtures.

The simplest expression for G' comes from assuming that the ternary mixture forms an ideal solution whence

$$G' = RT \sum_{i=1}^{3} n_i \, \ell n(n_i/n) \ , \qquad (5.6)$$

which is just (-T) times the entropy for random mixing. The discussion of concentration fluctuations on the

basis of (5.6) and (5.2) was given in Chapter 4. Eqn. (5.6) is valid when (a) the effects of differences in sizes of the various constituents in the mixture can be ignored and (b) the differences ω_{ij} (defined below) in the interactions between the different species are zero. If we retain the assumption (a) and treat the interactions ω_{ij} to be small, then we have conditions under which the theory of regular solutions in the zeroth approximation or the conformal solution approximation is valid. G' then is just a straightforward generalisation of (3.24) to a ternary mixture and is given by [see, for example, Longuet-Higgins (1951)]

$$G' = RT \sum n_i \ln(n_i/n) + \sum_{i<j} \sum (n_i n_j/n)\omega_{ij} \qquad (5.7)$$

where $i,j = 1,2,3$ and ω_{ij} ($\equiv 0$ for $i = j$) are the interaction energies defined in the usual way, for example, $2\omega_{12} = 2\omega_{AB} - \omega_{AA} - \omega_{BB}$ etc. For brevity, we shall refer to (5.7) as the conformal solution approximation or simply approximation (a).

The effects of differences in sizes between A, B and $A_\mu B_\nu$ are more difficult to take into account. A simple approximate expression for G', in similar vein to (5.7), is that due to Flory (1942, 1953), well known in polymer physics, namely,

$$G' = RT \sum n_i \ln \phi_i + \sum_{i<j} \sum n_i \phi_j \chi'_{ij} , \qquad (5.8)$$

where ϕ_i is the concentration by volume of the ith species in the mixture and χ'_{ij} ($\equiv 0$ if $i = j$) are interaction energies (similar to ω_{ij} in Eqn. (5.7)) between the different species, and are (RT) times the χ_{ij} defined in Flory (1953). The first term in (5.8) is the expression, in Flory's approximation (see also below), for (-T) times the entropy of mixing three species whose molecules differ appreciably in volume from one another. If these volumes are all equal, then $\phi_i = n_i/n$ and (5.8) becomes identical with (5.7). We make here a further simplification of (5.8) by assuming that the volume per atom of A and B atoms is nearly the same, say v, and the volume of $A_\mu B_\nu$ is $(\mu+\nu)v$. [This assumption is essentially similar to that often made in quasi-lattice models of monomer-polymer solutions and is of course only approximately true†; see below]. Then

$$\phi_1 = n_1/\mathcal{N} \quad , \quad \phi_2 = n_2/\mathcal{N} \quad , \quad \phi_3 = (\mu+\nu)n_3/\mathcal{N} \quad . \tag{5.9}$$

With (5.9), expression (5.8) becomes

$$G' = RT[n_1 \ln(n_1/\mathcal{N}) + n_2 \ln(n_2/\mathcal{N}) + n_3 \ln((\mu+\nu)n_3/\mathcal{N})] + \sum_{i<j}\sum (n_i n_j/\mathcal{N})v_{ij} \quad , \tag{5.10}$$

---

† For an account of the quasi-lattice models, see, for example, Guggenheim (1952) or Prigogine (1957).

where we have set $v_{12} \equiv \chi'_{12}$, $v_{13} = (\mu+\nu)\chi'_{13}$, $v_{23} = (\mu+\nu)\chi'_{23}$. We shall refer to (5.10), for brevity, as Flory's approximation or approximation (b). We note, as is well known, that the combinatorial term [the term proportional to RT] in (5.10) follows also from the quasi-lattice models of monomer-polymer solutions if the coordination number z is taken to be infinite†.

In the following we shall use the approximations (a) and (b) above, in conjunction with (5.2), to calculate the thermodynamic properties of some compound forming systems. Each of these approximations contains four parameters, g and ω_{ij} (or v_{ij}). There exist, of course, higher approximations to G' than (5.7), (5.8) or (5.10) in the literature, but these are involved and contain, in general, additional parameters [coordination number, surface to volume ratio for polymer molecules (chemical complexes) etc.] and will not be pursued here.

---

† See, for example, Guggenheim (1952), Eqns. (10.10.4) and (10.10.1). Note that in these equations for our problem, $r_1 = 1$, $r_2 = 1$, $r_3 = \mu+\nu$. Note also that N_i of Guggenheim are n_i in our notation, and the combinatorial term in G' is just $-T \sum_i n_i \Delta_M S$. In the limit $z \to \infty$, $q_3 \to \mu+\nu$ and the (10.10.4) gives the combinatorial term in (5.10). In practice, the difference between the latter and (10.10.4) is quite small for $z > 8$ or 10.

It may at first sight seem surprising that we should consider the approximation (a) at all, since even if the sizes of A and B atoms are equal, the size of $A_\mu B_\nu$ will not be that of A or B. However, we should recall firstly from §3.4, that the conformal (or regular) solution theories are generally considered to be reasonable for volumes of the different species differing by up to 100%. Secondly, the bond length between A and A, B and B or A and B may be different (less!) when both atoms of the pair are in the chemical complex than when one or both of the atoms do not belong to the chemical complex. Hence, since approximation (b) is also only an approximation to a truly complex situation, and μ and ν are small integers in our problem, it was thought desirable to make calculations on both the approximations (a) and (b) above. We comment later on the extent to which the two approximations agree with experiment.

5.3 Expressions for Various Thermodynamic Quantities

5.3.1 Approximation (a)

Combining Eqn. (5.7) with (5.2), the free energy of mixing G_M for the compound forming binary alloy is

$$G_M = - n_3 g + RT \sum_{i=1}^{3} n_i \ln(n_i/n) + \sum_{i<j} \sum (n_i n_j/n)\omega_{ij} \quad (5.11)$$

The equilibrium number of chemical complexes is given by the condition (5.5). This gives, on using (5.1) and after some rearrangement of terms, the equation

$$n_1^{\mu} n_2^{\nu} = (n_3 n^{\mu+\nu-1}) K e^{Y} \tag{5.12}$$

where

$$K = \exp[-g/RT] \tag{5.13}$$

and

$$\begin{aligned} Y = {} & (\omega_{12}/RT)\{(\mu+\nu-1)(n_1 n_2/n^2) - \mu(n_2/n) - \nu(n_1/n)\} \\ & + (\omega_{13}/RT)\{(\mu+\nu-1)(n_1 n_3/n^2) - \mu(n_3/n) + (n_1/n)\} \\ & + (\omega_{23}/RT)\{(\mu+\nu-1)(n_2 n_3/n^2) - \nu(n_3/n) + (n_2/n)\}. \end{aligned} \tag{5.14}$$

On eliminating n_1, n_2 and n in (5.12) and (5.14) from (5.1), Eqn. (5.12) is seen to be an equation in the single unknown n_3. When the solution of (5.12) for n_3, and the corresponding values of n_1, n_2 and n are substituted into (5.11) one obtains the equilibrium free energy of mixing G_M for comparison with experiment. In the following, to avoid cumbersome notation, we shall continue to denote the equilibrium values of n_3, n_1, n_2, etc. by the same symbols. We note that the differentiation of G_M with respect to a variable say T, at equilibrium can be written as

$$(\partial G_M/\partial T)_{P,c,\mathcal{N}} = (\partial G_M/\partial n_3)_{T,P,c,\mathcal{N}} (\partial n_3/\partial T)_{P,c,\mathcal{N}} +$$

$$+ (\partial G_M/\partial T)_{P,c,n_3,\mathcal{N}}$$

$$= (\partial G_M/\partial T)_{P,c,n_3,\mathcal{N}} \qquad (5.15)$$

by virtue of the equilibrium condition (5.5). Similar results apply for differentiations with respect to c or P.

Using (5.11) and (5.15), the expression for the heat of mixing H_M is

$$H_M = G_M - T(\partial G_M/\partial T)_P \qquad (5.16a)$$

$$= -n_3\left[g - T(\frac{\partial g}{\partial T})_P\right] + \sum_{i<j}\sum (\frac{n_i n_j}{n})\left[\omega_{ij} - T(\frac{\partial \omega_{ij}}{\partial T})_P\right] \qquad (5.16b)$$

and the entropy of mixing $S_M = (H_M - G_M)/T$.

The concentration fluctuations S_{CC} are given by (2.39), namely,

$$S_{CC} = \mathcal{N}RT/(\partial^2 G_M/\partial c^2)_{T,P,\mathcal{N}} \qquad (5.17)$$

Hence differentiating (5.11) twice with respect to c and using (5.1) and (5.12), one may obtain after some algebra

$$S_{CC} = \frac{s_{CC}}{1 + \mathcal{D} s_{CC}} \,. \qquad (5.18)$$

Here

$$s_{cc} = \mathcal{N}\left[\sum_{i=1}^{3} (n_i')^2/n_i - (n')^2/n\right]^{-1}, \qquad (5.19)$$

$$\mathcal{S} = \frac{2n}{\mathcal{N}RT} \cdot \sum_{i<j} \sum \omega_{ij} \left(\frac{n_i}{n}\right)' \left(\frac{n_j}{n}\right)' \qquad (5.20)$$

where a prime denotes differentiation with respect to c. The expression for n_3' is obtained by straightforward differentiation of (5.12) using (5.1) and noting that $n_1' = \mathcal{N} - n_3'$ etc. In (5.20)

$$(n_i/n)' = (n_i'n - n'n_i)/n^2 .$$

Finally, as mentioned previously, experimentally S_{cc} is determined from the measured activities. If a_A denotes the activity of the component A in the mixture, one has from (2.41) remembering that $a_A \equiv a_1$,

$$S_{cc} = (1-c)a_A/a_A' . \qquad (5.21)$$

In terms of G_M, a_A is given by Eqn. (2.40), i.e.

$$RT \ln a_A = \left(\frac{\partial G_M}{\partial N_A}\right)_{T,P,N_B} = \frac{1}{N}\left(G_M + (1-c)\left(\frac{\partial G_M}{\partial c}\right)_{T,P,N}\right) . \qquad (5.22)$$

With G_M given by (5.11), Eqn. (5.22) gives, on using (5.1) and (5.5),

$$\ln a_A = \ln\left(\frac{n_1}{n}\right) + \frac{1}{RT}\left[\left(\frac{n_2}{n}\right)\omega_{12} + \left(\frac{n_3}{n}\right)\omega_{13} - \sum_{i<j} \sum \left(\frac{n_i}{n}\right)\left(\frac{n_j}{n}\right)\omega_{ij}\right] . \qquad (5.23)$$

Using (5.23), the expressions (5.21) and (5.18) for S_{cc} may be verified to be equivalent to one another.

The expression (5.18) has certain advantages in deducing the limiting behaviours of S_{CC}, considered in §5.4, from theory.

5.3.2 Approximation (b)

In this approximation G' is given by (5.10). Hence using (5.2), we obtain†

$$G_M = - n_3 g + RT\left[n_1 \ln \frac{n_1}{\mathcal{N}} + n_2 \ln \frac{n_2}{\mathcal{N}} + n_3 \ln \frac{(\mu+\nu)n_3}{\mathcal{N}}\right] + \sum_{i<j}\sum (n_i n_j/\mathcal{N}) v_{ij} \quad . \tag{5.24}$$

Using (5.5) in (5.24), the equilibrium value of n_3 is given by the equation

---

† An expression essentially similar to (5.24) for G_M has been recently derived in another manner by Takeuchi et. al. (1973) for the case where one of μ, ν is unity. Takeuchi et. al. use this to calculate n_3 as a function of concentration for Cu-Sn and Cu-In. The interaction parameters in this work were determined from the observed values of H_M neglecting in the expression for H_M the possible temperature dependence of v_{ij}. No comparison of other thermodynamic quantities is made in this work. (A calculation made by us for Cu-Sn with their parameters gives substantial disagreement with experiment for S_{CC}. See also §5.5).

$$n_1^{\mu} n_2^{\nu} = (n_3 \mathcal{N}^{\mu+\nu-1})\ K' e^{Z} \tag{5.25}$$

where

$$K' = K(\mu+\nu)\exp[-(\mu+\nu-1)] \tag{5.26}$$

$$Z = (\mathcal{N} RT)^{-1}[(n_1-\mu n_3)v_{13}+(n_2-\nu n_3)v_{23}-(\mu n_2+\nu n_1)v_{12}] \tag{5.27}$$

and K is given by (5.13). Next remembering that the heat of mixing and activity are related to G_M by (5.16a) and (5.22), one obtains for this case

$$H_M = -n_3\left[g - T\left(\frac{\partial g}{\partial T}\right)_P\right] + \sum_{i<j}\sum \frac{n_i n_j}{\mathcal{N}}\left[v_{ij} - T\left(\frac{\partial v_{ij}}{\partial T}\right)_P\right] \tag{5.28}$$

$$\ln a_A = \ln \frac{n_1}{n} + 1 + \ln \frac{n}{\mathcal{N}} - \frac{n}{\mathcal{N}} + \frac{1}{\mathcal{N} RT}(n_3 v_{13} + n_2 v_{12})$$

$$- \frac{1}{\mathcal{N}^2 RT} \sum_{i<j}\sum n_i n_j v_{ij} \ . \tag{5.29}$$

Finally, using (5.17) in (5.24), one finds that S_{CC} may again formally be written in the form (5.18), but with s_{CC} and $\mathcal{D}$ in it now given by

$$s_{CC} = \mathcal{N}\left(\sum_{i=1}^{3} (n_i')^2/n_i\right)^{-1}$$

$$\mathcal{D} = (2/\mathcal{N}^2 RT) \sum_{i<j}\sum n_i' n_j' v_{ij} \ . \tag{5.30}$$

5.4 Expressions for S_{CC} for Two Limiting Cases

Of the thermodynamic functions G_M, a_A and S_{CC}, the concentration dependence of S_{CC} exhibits the most interesting and varied features (see Figs. 5.1-5.3). To have a qualitative understanding of these features it is instructive to consider two limiting cases for which analytic expressions for S_{CC} may be obtained.

The first limiting case refers to situations where there is a very strong tendency to form chemical complexes, that is, $g/RT \gg 1$ or $K \ll 1$. We therefore consider the limit $K \to 0$. Considering first the approximation (a), we see that in the equilibrium Eqn. (5.12), $K \to 0$ implies also $K \exp[Y] \to 0$, since (ω_{ij}/RT) are by assumption small finite numbers. Then, if $n_3 \neq 0$, Eqn. (5.11) implies that either $n_1 \to 0$ or $n_2 \to 0$. One then has, using (5.1),

$$n_3 \to \mathcal{N}c/\mu \qquad \text{for} \quad 0 < c \leq \mu/(\mu+\nu) \ , \tag{5.31}$$

$$n_3 \to \mathcal{N}(1-c)/\nu \qquad \text{for} \quad \mu/(\mu+\nu) \leq c < 1 \ . \tag{5.32}$$

In the limit (5.31) $n_1 \to 0$, and one may show[†] also that

---

[†] To see this, let $n_3 = (\mathcal{N}c/\mu) - \Delta n_3$. Substitute this in (5.12). Then using (5.1), remembering that $K \ll 1$, and retaining lowest order terms in Δn_3, one finds that Δn_3 and hence $n_1 \simeq \mu \Delta n_3$ are proportional to a positive power of K. Hence as $K \to 0$, n_1, n_1' and $(n_1')^2/n_1$ tend to zero.

$n_1' \to 0$ and $(n_1')^2/n_1 \to 0$. Using this result and (5.31) and Eqns. (5.1) in the expressions (5.19) and (5.20) for s_{CC} and $\mathcal{D}$, one obtains straightforwardly for $(0 < c \leq \mu/(\mu+\nu))$

$$s_{CC}^{(a)} = (c/\mu)[\mu - c(\mu+\nu)][\mu - (\mu+\nu-1)c]$$

$$\mathcal{D}^{(a)} = -2(\omega_{23}/\mu^2 RT)(\mathcal{N}/n)^3, \quad n = \mathcal{N}[1 - c(\mu+\nu-1)/\mu]. \quad (5.33)$$

The index 'a' signifies that these expressions are for the approximation (a). $s_{CC}^{(a)}$ then is of course

$$s_{CC}^{(a)} = s_{CC}^{(a)}[1 + \mathcal{D}^{(a)} s_{CC}^{(a)}]^{-1} \quad . \quad (5.34)$$

Similarly from (5.32), for the concentration range $\mu/(\mu+\nu) \leq c < 1$,

$$s_{CC}^{(a)} = \nu^{-1}(1-c)[\nu - (1-c)(\mu+\nu)][\nu - (1-c)(\mu+\nu-1)]$$

$$\mathcal{D}^{(a)} = -2(\omega_{13}/\nu^2 RT](\mathcal{N}/n)^3, \quad n = \mathcal{N}[1 - (1-c)(\mu+\nu-1)/\nu]. \quad (5.35)$$

The solutions (5.31) and (5.32) and hence the corresponding expressions for s_{CC} and $\mathcal{D}$ are not valid in the limits $c \to 0$ and $c \to 1$ respectively. For these cases n_3 itself tends to zero and the equilibrium Eqn. (5.12) requires more careful analysis. By following steps similar to those given in §4.4 for the case $\omega_{ij} = 0$, one may show that for $c \ll 1$, the equilibrium Eqn. (5.12) has the solution

$$n_3 = \nu c\alpha + O(c^2) \quad , \quad \text{for} \quad \mu = 1 \tag{5.36a}$$

$$n_3 = \nu c^{\mu}/K_a + O(c^{\mu+1}) \quad , \quad \text{for} \quad \mu \geq 2 \tag{5.36b}$$

where

$$K_a = K \exp[(\omega_{23} - \mu\omega_{12})/RT] \quad , \quad \alpha = (1+K_a)^{-1} \quad . \tag{5.37}$$

The exponent in (5.37) is just the value of Y [Eqn. (5.14)] at c = 0. The solution (5.36b) is valid when both (see §4.4),

$$c << 1 \quad \text{and} \quad c << (K_a/\mu)^{1/(\mu-1)} . \tag{5.38}$$

As may be verified, the solutions (5.36) are sufficient to determine $S_{CC}^{(a)}$ to order c^2 and one obtains after some algebra

$$S_{CC}^{(a)} = c - c^2[1 + 2\nu\alpha + \frac{2}{RT}(\omega_{13}\alpha(1-\alpha) - \omega_{23}\alpha - \omega_{12}(1-\alpha))] + O(c^3) \quad \text{for} \quad \mu = 1 , \tag{5.39}$$

and

$$S_{CC}^{(a)} = c - c^2[1 - (2/K_a) - 2\omega_{12}/RT] + O(c^3), \quad \text{for} \quad \mu = 2 \tag{5.40a}$$

$$= c - c^2[1 - 2\omega_{12}/RT] + O(c^3), \quad \text{for} \quad \mu \geq 3 . \tag{5.40b}$$

The expansions (5.40) are valid when both the inequalities in (5.38) are satisfied. To obtain similar expansions near c = 1, replace in Eqns. (5.36)-(5.40), c by 1-c and make the interchange $\mu \rightleftarrows \nu$ and $\omega_{23} \rightleftarrows \omega_{13}$. Eqns. (5.39)-(5.40) demonstrate that for sufficiently

small c, $S_{CC} = c$ in all cases. The expansions are carried to order c^2 here, since as discussed earlier, the value at $c = 0$ of one of the Faber-Ziman partial structure factors depends on $[d^2S_{CC}/dc^2]_{c=0}$. Similar remarks with appropriate changes apply to the region $c \to 1$.

We note that in the special case where all $\omega_{ij} = 0$, so that G' is given by (5.6), the various expressions (5.33)-(5.35), (5.39) and (5.40) for $S_{CC}^{(a)}$ reduce to those given in Chapter 4, as they should.

In Flory's approximation (approximation (b)), for $K \to 0$, n_3 are again given by (5.31) and (5.32). For S_{CC}, $\mathscr{D}$ etc. one then obtains, using (5.30),

$$s_{CC}^{(b)} = \frac{\mu c(\mu-(\mu+\nu)c)}{\mu+(\mu+\nu)(\mu+\nu-1)c} \quad , \quad \mathscr{D}^{(b)} = -\frac{2(\mu+\nu)}{\mu^2 RT} v_{23} \quad , \quad (5.41)$$

for $0 < c \leq \mu/(\mu+\nu)$, and

$$s_{CC}^{(b)} = \frac{\nu(1-c)(\nu-(\mu+\nu)(1-c)}{\nu+(\mu+\nu)(\mu+\nu-1)(1-c)} \quad , \quad \mathscr{D}^{(b)} = -\frac{2(\mu+\nu)}{\nu^2 RT} v_{13} \quad , \quad (5.42)$$

for $\mu/(\mu+\nu) \leq c < 1$. Finally the low c expansions for this case are

$$s_{CC}^{(b)} = c-c^2\{(1+\nu\beta)^2+(2/RT)[-v_{12}(1-\beta)(1+\nu\beta)+(1-\beta)\beta v_{13} - (1+\nu\beta)\beta v_{23}]\} + O(c^3) \quad , \quad \text{for } \mu = 1 \quad , \quad (5.43)$$

$$= c-c^2[1-(3/K_b)-2v_{12}/RT] + O(c^3) \quad , \quad \text{for } \mu = 2 \quad , \quad (5.44)$$

$$= c-c^2[1-2v_{12}/RT] + O(c^3) \quad , \quad \text{for } \mu \geq 3, \quad (5.45)$$

where

$$K_b = K'\exp[(v_{23}-\mu v_{12})/RT] \ , \quad \beta = (1+K_b)^{-1} \ . \qquad (5.46)$$

The expressions (5.44)-(5.45) are valid only when both $c \ll 1$ and $c \ll (K_b/\mu)^{1/(\mu-1)}$. The expansions near $c = 1$ are obtained from (5.43)-(5.46) by interchanging $c \overset{+}{+} (1-c)$, $\mu \overset{+}{+} \nu$ and $v_{23} \overset{+}{+} v_{13}$.

The second limiting case refers to situations where there is only a very weak or no tendency to form chemical complexes, that is, $(g/RT) \ll 0$ or $K \gg 1$. As $K \to \infty$, an inspection of the equilibrium Eqn. (5.12) or (5.25) shows that in both the approximations (a) and (b), $n_3 \propto K^{-1}$. Hence as $K \to \infty$, n_3, n_3' and $(n_3')^2/n_3$ all tend to zero. Then since $n_1 \to \mathcal{N}c$, $n_2 \to \mathcal{N}(1-c)$ and $n \to \mathcal{N}$, we have for approximation (a), from Eqns. (5.18)-(5.20),

$$S_{CC} = \frac{c(1-c)}{1-2(\omega_{12}/RT)c(1-c)} \ , \quad K \to \infty \ . \qquad (5.47)$$

The approximation (b) gives the same result with ω_{12} replaced by v_{12}. The expression (5.47) for S_{CC} is the same as for a binary regular solution in the zeroth approximation, as is to be expected.

From the various expressions given above we infer the following regarding the concentration dependence of S_{CC}: (1) In every case S_{CC} starts from zero at $c = 0$ with the slope unity and ends at zero with the

slope -1 at c = 1. (2) If K << 1, then in the K → 0 limit S_{CC} is again zero at the chemical composition $c_c \equiv \mu/(\mu+\nu)$ - see Eqns. (5.33)-(5.35) and (5.41)-(5.42). Thus S_{CC} has two maxima, one in the concentration range $0 < c < c_c$ and the other in the range $c_c < c < 1$. The height and position of these maxima depend, apart from the values of K(<<1), μ and ν, on the magnitudes and signs of ω_{23} and ω_{13} (or v_{23} and v_{13}) respectively. (3) In the opposite limit K → ∞, S_{CC} has just one maximum which occurs at $c = \frac{1}{2}$, its height being determined by the sign and magnitude of ω_{12} (or v_{12}). We note that an infinite S_{CC}, which can happen for positive ω_{ij} (or v_{ij}) implies phase separation and our treatment applies in such cases only at temperatures above the critical temperature for phase separation or far away from the critical composition.

The results of the detailed calculations show that the K → 0 limit expressions for n_3 and S_{CC} form a good first approximation if $g \gtrsim 3(\mu+\nu)RT$. Remembering (5.31) and (5.32) this implies that, with G_M negative, $|G_M(c_c)/\mathcal{N}| \gtrsim 3RT$. Two of the systems (Mg-Bi and Tl-Te) examined below belong to this class at the temperatures under consideration. For the other two systems $|G_M(c_c)/\mathcal{N}RT|$ is not so large and the behaviour of S_{CC} is intermediate between that expected from the K → 0 and K → ∞ limits. As the temperature increases

K(=exp[-g/RT]) may be expected to increase, so that, for a given system, with increasing temperatures, S_{CC} will tend towards the behaviour given by (5.47) and eventually towards $S_{CC} = c(1-c)$ appropriate to an ideal solution†.

5.5 Numerical Results

In order to apply the various equations of §5.3 to a specific system, we have to solve numerically the equilibrium Eqn. (5.12) and at the same time determine the parameters g (or K) and ω_{ij} from the observed data on the free energy of mixing G_M, using (5.11). (We explicitly confine our remarks to approximation (a) - the procedure followed for approximation (b) was similar.)

---

† We note that the fact that the two approximations (a) and (b) give the same limiting behaviour for S_{CC} at high temperatures is a consequence of the assumption that in both the approximations the atomic volumes of pure A and B liquids are taken to be not too different from one another. If this is not the case one should use for G' expression (5.8) and then the limiting behaviour of S_{CC} would be given by the expression which one obtains by considering the binary mixture in Flory's approximation, i.e. Eqn. (3.44) of Chapter 3.

For two of the molten systems considered, namely Mg-Bi and Tl-Te which in the solid state form highly stable compounds Mg_3Bi_2 ($\mu = 3, \nu = 2$) and Tl_2Te ($\mu = 2, \nu = 1$), $|G_M(c_c)/\mathcal{N}RT| > 3$ at the temperatures of observation. For these cases, therefore, we took as a starting approximation that n_3 is given by (5.31) and (5.32) which is appropriate for $K << 1$. Then at the chemical composition $c_c = \mu/(\mu+\nu)$, $G_M \simeq -n_3 g$, which gives a starting value for g or K. With n_3 still given by (5.31) and (5.32) and g as determined above, the expression for G_M, for $c < c_c$, contains the single unknown parameter ω_{23} (since $n_1 \simeq 0$). A value of ω_{23} was thus determined from the observed data on G_M at an intermediate concentration between 0.1 and c_c. Similarly ω_{13} was determined from the observed value of G_M at a concentration intermediate between c_c and 0.9. It may be seen, using expressions (5.31), (5.32) and (5.36) for n_3, that for systems with $K << 1$, ω_{12} affects G_M significantly only for $\mu \geq 2$ and $c << 1$ as determined by the second inequality in (5.38) [and similarly for $\nu \geq 2$ in the region $1-c << 1$]. Since this implies c to be less than 0.001 for Mg-Bi and Tl-Te systems, ω_{12} could not be determined from the experimental data on G_M. Finding that any reasonable choice of ω_{12} ($\sim RT$) affects the values of other parameters only slightly we set in our calculations $\omega_{12} = 0$.

With the above starting choice of g, and ω_{ij}, the equilibrium Eqn. (5.12) was solved for n_3 and the parameters were adjusted in the light of these values of n_3 to obtain a good fit for G_M. The final choice of the parameters is given in Table 5.1(a).

For the other two systems considered, namely Ag-Al and Cu-Sn, which were assumed to form chemical complexes Ag_3Al ($\mu = 3$, $\nu = 1$) and Cu_4Sn ($\mu = 4$, $\nu = 1$) respectively, $|G_M/\mathcal{N}RT| \simeq 1.2$ and 0.9 at the respective chemical composition. This implies smaller values of g/RT (larger K or weaker tendency to form chemical complexes) than for Mg-Bi and Tl-Te. As a starting approximation we took g to be $-(\mu+\nu)G_M(c_c)/\mathcal{N}$. Unlike the case of Mg-Bi and Tl-Te, the calculations had to be made for several different choices of parameters before a good fit for G_M could be obtained. We did not attempt any mean square deviation tests to decide on the best fit so that the parameters given in Table 5.1 are to be regarded as reasonable choices rather than necessarily the best possible ones.

The parameters similarly found for approximation (b) for the four systems are given in Table 5.1(b).

The results of calculation of G_M together with the experimental data for the four systems are plotted in Figs.5.1 (a-d). The variation of n_3 with concentration is also shown here for each case. Figs.5.2(a-d)

Table 5.1

Interaction parameters for the systems Tl-Te, Mg-Bi, Ag-Al and Cu-Sn in the approximations (a) and (b).

(a): Approximation (a)

System	Temp. (°K)	K (Eqn.(5.13))	g/RT	$\omega_{12}/RT^{\dagger}$	ω_{13}/RT	ω_{23}/RT
Tl-Te	873	2×10^{-5}	10.82	0	1.95	-4.0
Mg-Bi	973	1.25×10^{-7}	15.9	0	-4.8	-3.0
Ag-Al	1173	0.04	3.2	-0.95	-0.3	-2.7
Cu-Sn	1593	0.08	2.5	-0.9	0	-2.0

(b): Approximation (b)

System	Temp. (°K)	K (Eqn.(5.26))	g/RT	$v_{12}/RT^{\dagger}$	v_{13}/RT	v_{23}/RT
Tl-Te	873	8×10^{-6}	10.84	0	3.6	-4.0
Mg-Bi	973	5×10^{-9}	16.7	0	-1.0	0.8
Ag-Al	1173	0.004	3.9	-0.8	2.5	-1.5
Cu-Sn	1593	0.01	2.2	-0.8	2.0	-2.0

† See discussion in the text regarding the choice of ω_{12} and v_{12} for Tl-Te and Mg-Bi.

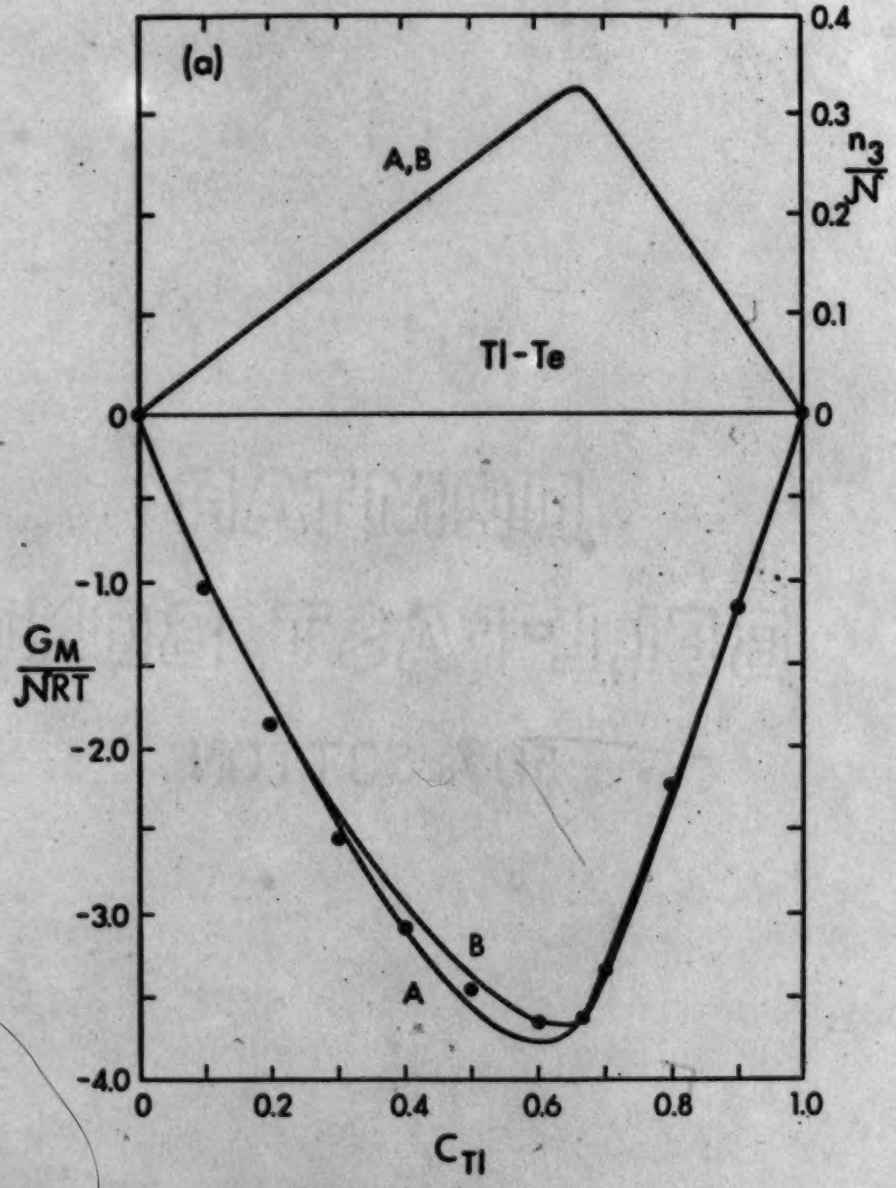

Fig. 5.1a. $G_M/\mathcal{N}RT$ and $n_3/\mathcal{N}$ as functions of concentration for Tl-Te. Curve A: conformal solution approximation; curve B: Flory's approximation - see text. • Experimental data for G_M taken from Nakamura and Shimoji (1971).

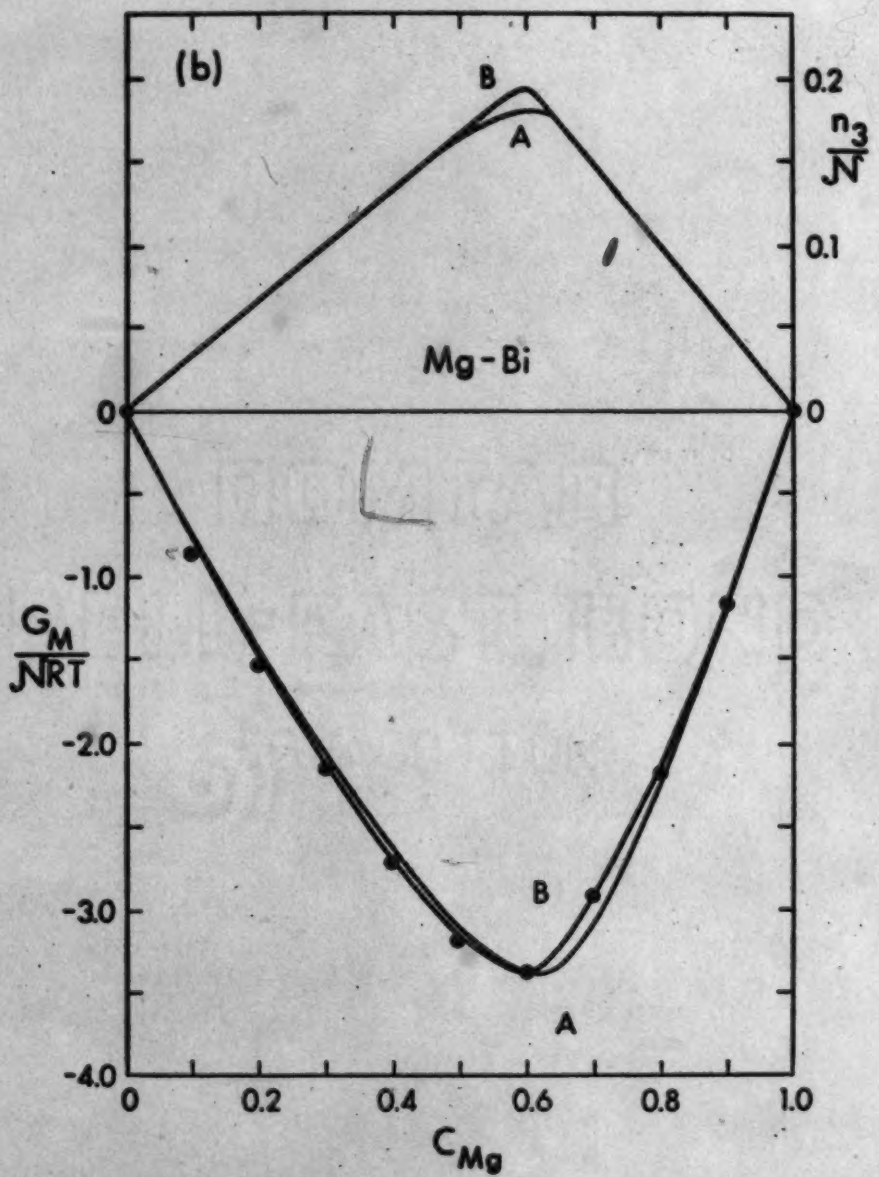

Fig. 5.1b. $G_M/\mathcal{N}RT$ and $n_3/\mathcal{N}$ as functions of concentration for Mg-Bi. Theoretical curves A and B as explained in Fig. 5.1a. • Experimental data for G_M taken from Hultgren et. al. (1963).

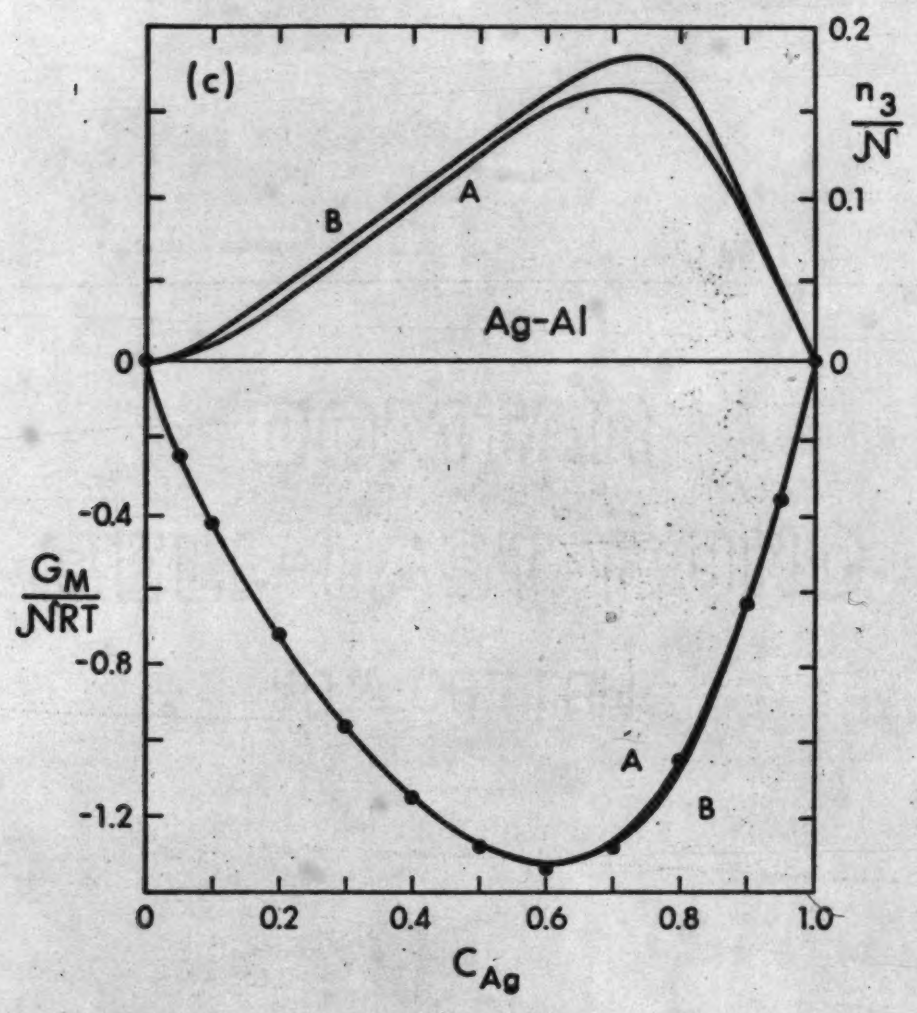

Fig. 5.1c. $G_M/\mathcal{N}RT$ and $n_3/\mathcal{N}$ as functions of concentration for Ag-Al. Theoretical curves A and B as explained in Fig. 5.1a. ● Experimental data for G_M taken from Wilder and Elliot (1960).

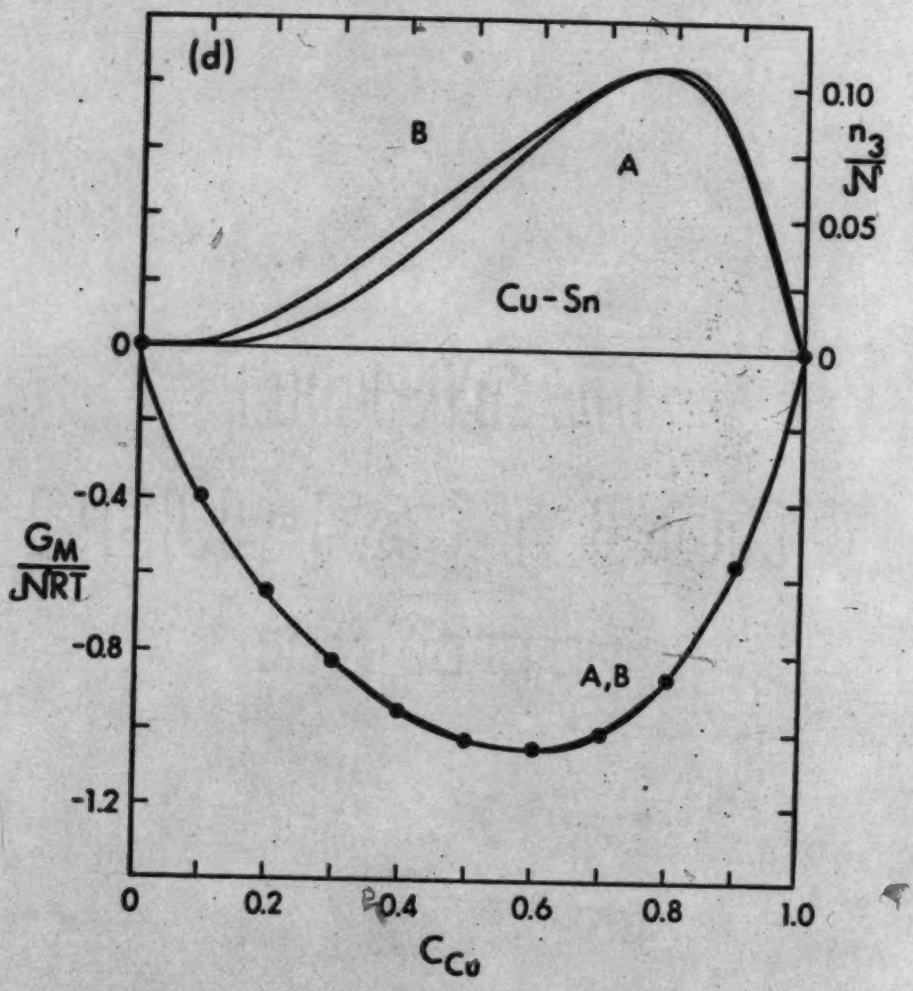

Fig. 5.1d. $G_M/\mathcal{N}RT$ and $n_3/\mathcal{N}$ as functions of concentration for Cu-Sn. Theoretical curves A and B as explained in Fig. 5.1a. ● Experimental data for G_M taken from Hager et.al. (1970).

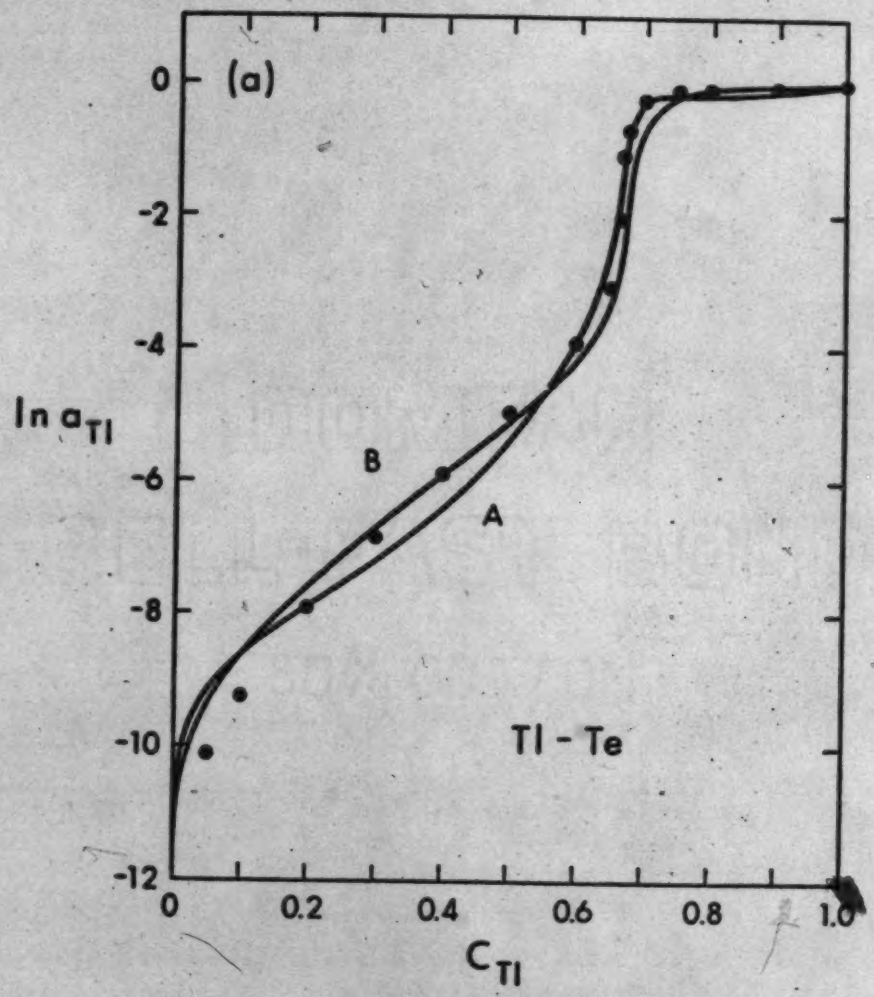

Fig. 5.2a. The logarithm of the activity, ln a_{Tl}, versus concentration for Tl-Te. Curve A: conformal solution approximation; curve B: Flory's approximation - see text. ● Experimental data from Nakumura and Shimoji (1971).

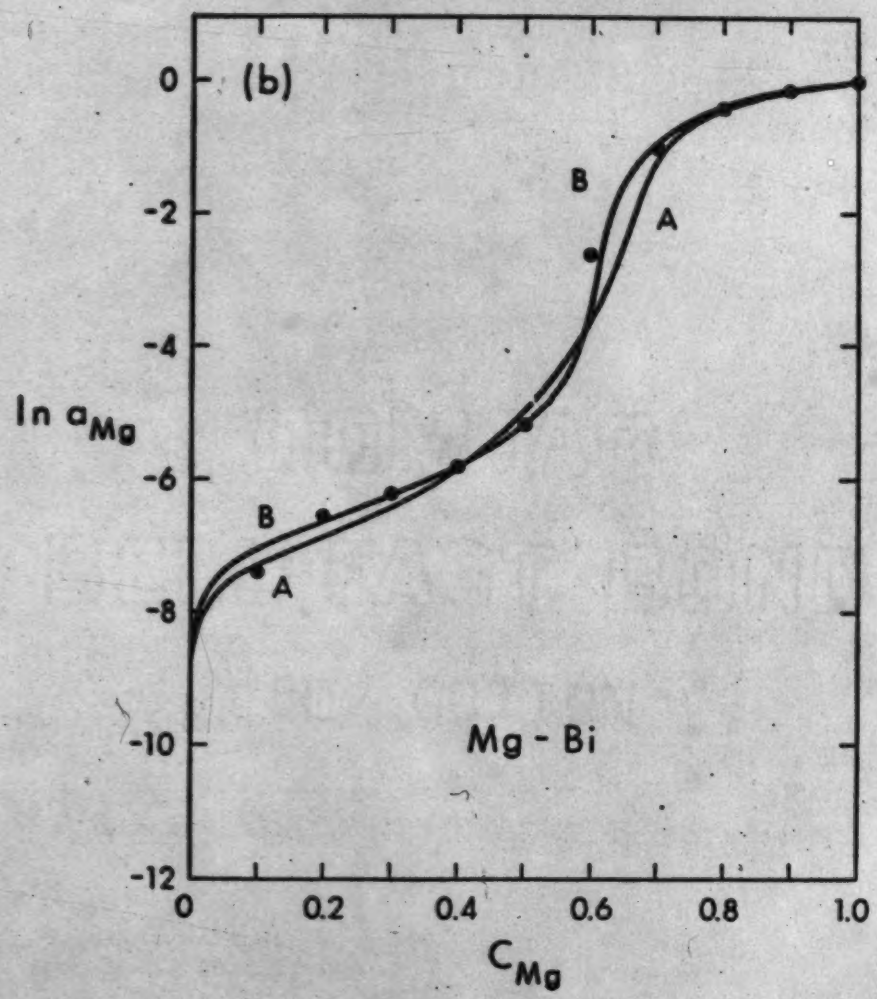

Fig. 5.2b. The logarithm of the activity, ln a_{Mg}, versus concentration for Mg-Bi. Theoretical curves as explained in Fig. 5.2a. • Experimental data from Hultgren et.al. (1963).

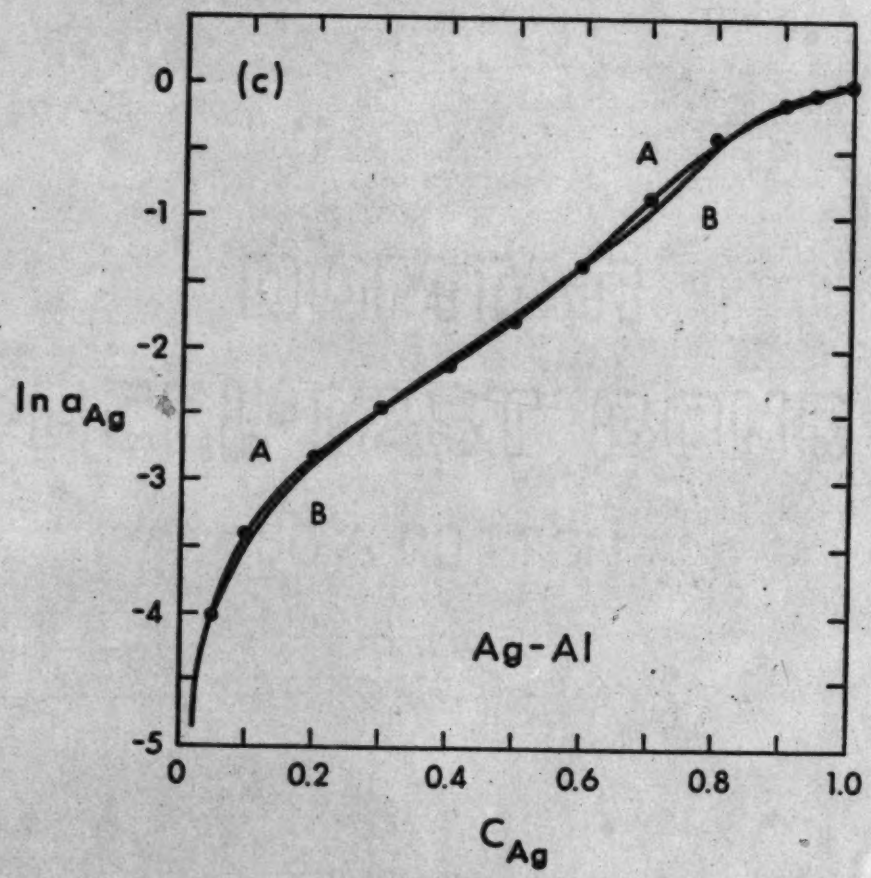

Fig. 5.2c. The logarithm of the activity, ln a_{Ag}, versus concentration for Ag-Al. Theoretical curves as explained in Fig. 5.2a. ● Experimental data from Wilder and Elliot (1960).

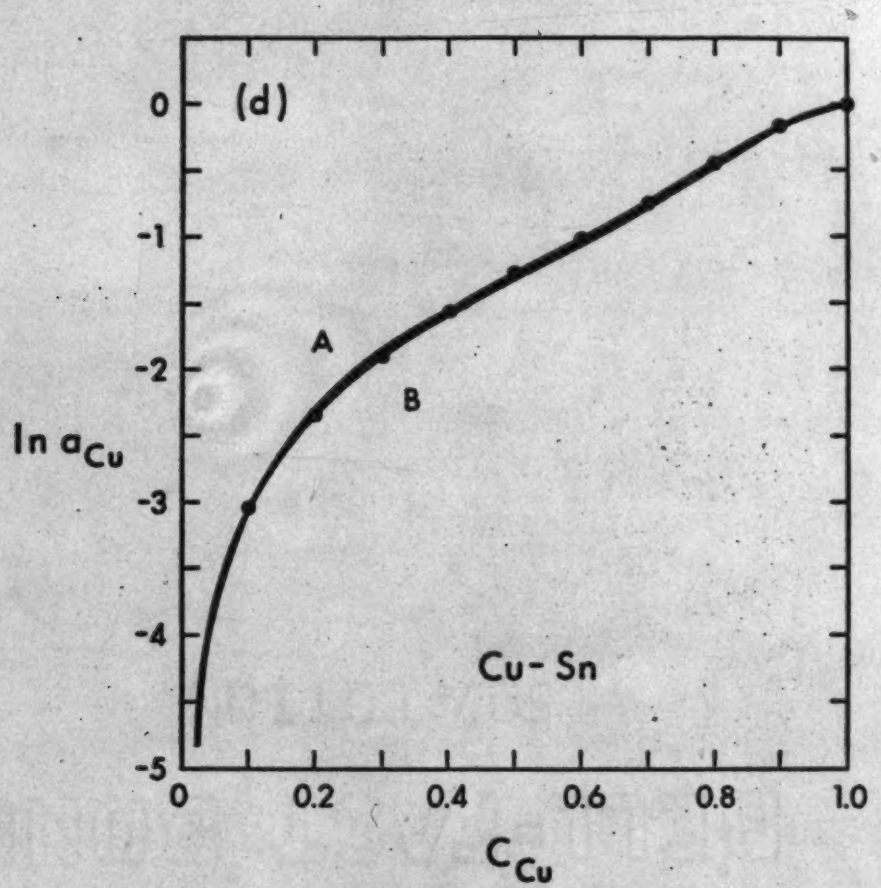

Fig. 5.2d. The logarithm of the activity, ln a_{Cu}, versus concentration for Cu-Sn. Theoretical curves as explained in Fig. 5.2a. • Experimental data from Hager et.al. (1970).

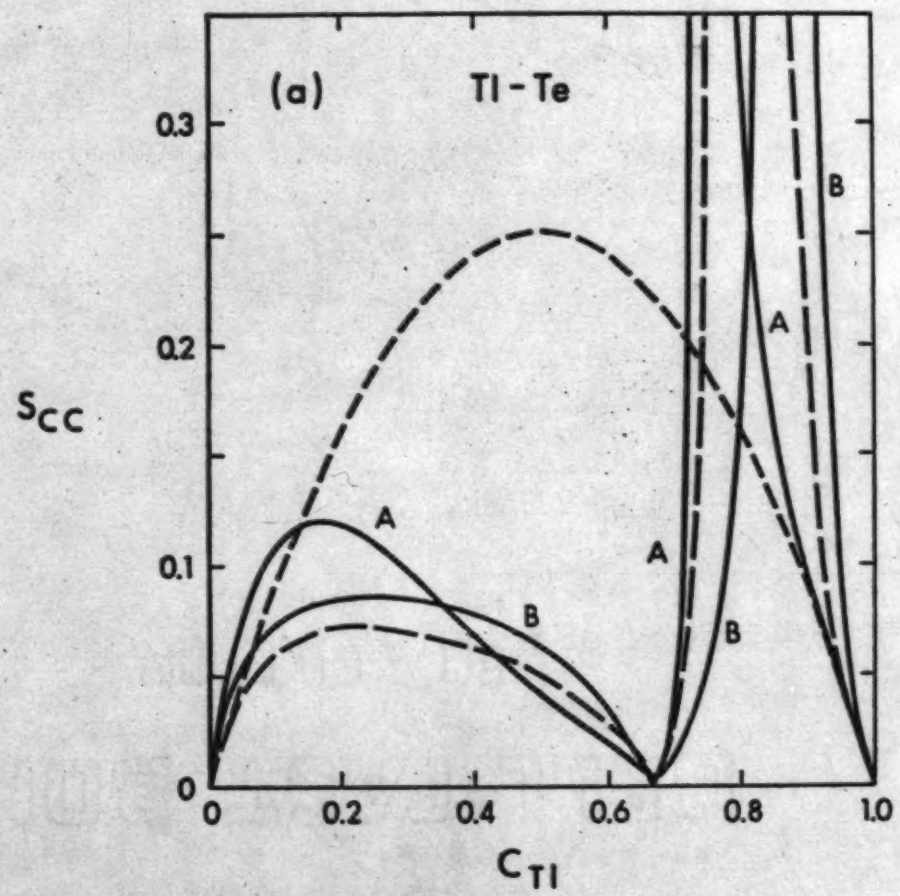

Fig. 5.3a. The concentration fluctuation S_{CC} versus concentration for Tl-Te. Solid curve A: conformal solution approximation; curve B: Flory's approximation - see text. — — — Experimental using data from Nakamura and Shimoji (1971). ----- $S_{CC}[=c(1-c)]$ for an ideal binary solution.

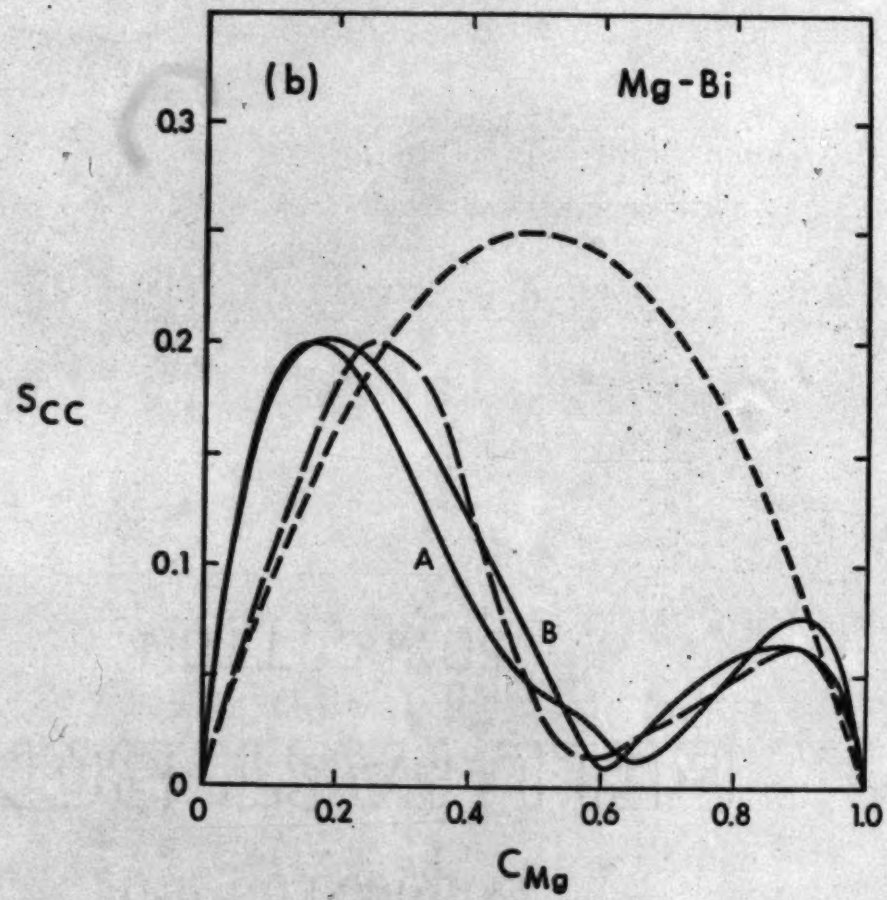

Fig. 5.3b. The concentration fluctuation S_{CC} versus concentration for Mg-Bi. Theoretical (solid) curves A and B as explained in Fig. 5.3a. — — — Experimental using data from Hultgren et,al.(1963). ----- S_{CC}[=c(1-c)] for an ideal binary solution.

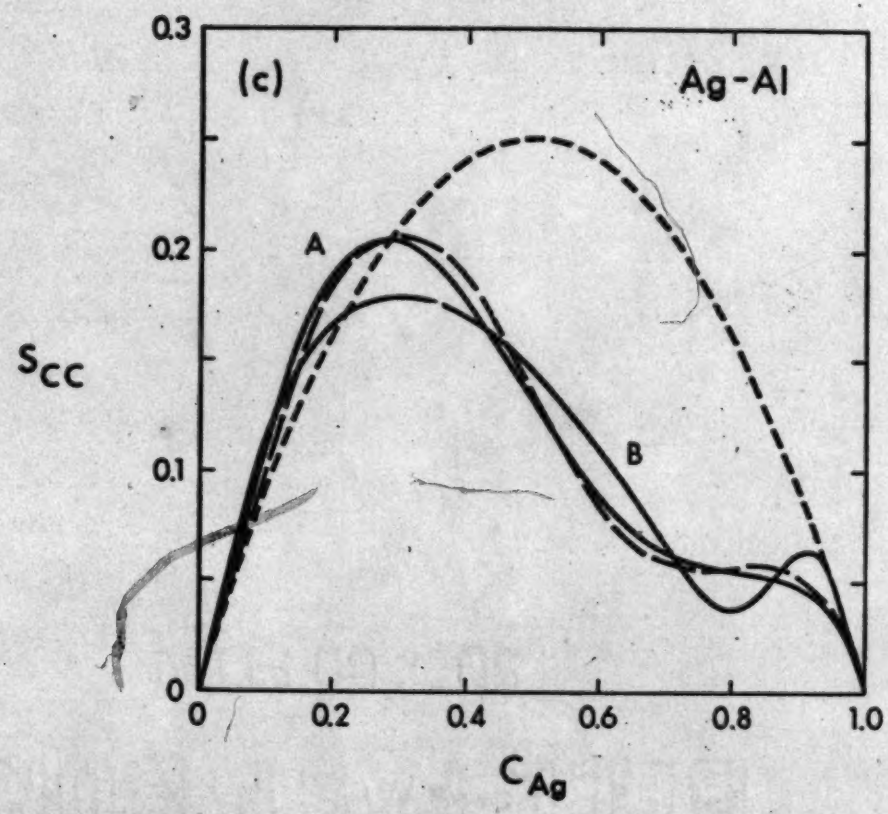

Fig. 5.3c. The concentration fluctuation S_{CC} versus concentration for Ag-Al. Theoretcial (solid) curves A and B as explained in Fig. 5.3a. — — — Experimental using data from Wilder and Elliot (1960). ----- S_{CC}[=c(1-c)] for an ideal binary solution.

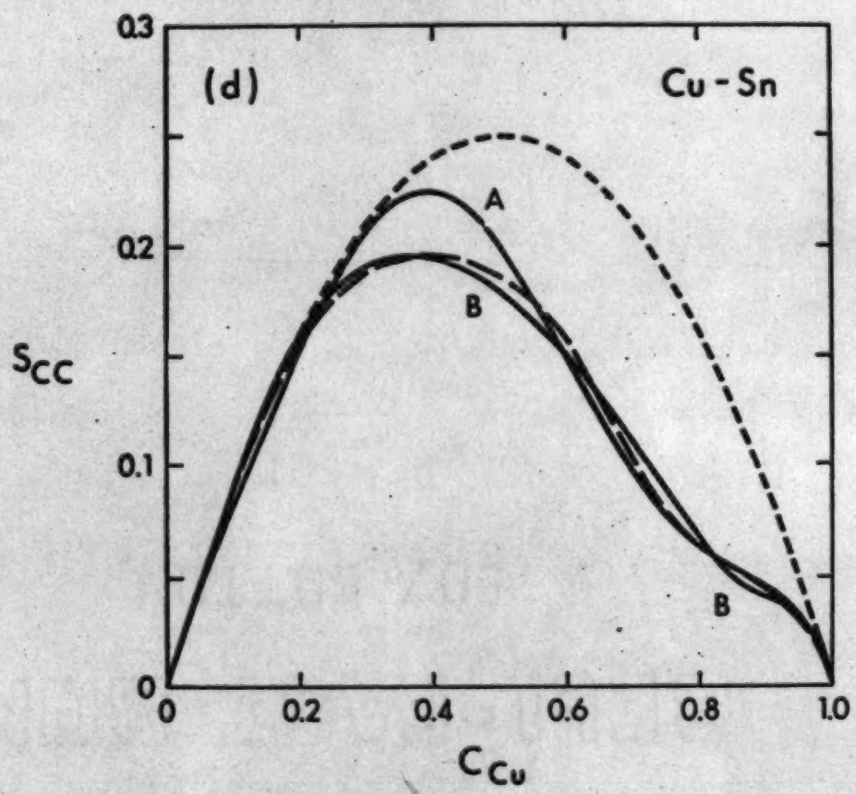

Fig. 5.3d. The concentration fluctuation S_{CC} versus concentration for Cu-Sn. Theoretical (solid) curves A and B as explained in Fig. 5.3a. — — — Experimental using data from Hager et.al. (1970). ----- S_{CC}[=c(1-c)] for an ideal binary solution.

compare the activities and Figs.5.3(a-d) the concentration fluctuations S_{CC}. For Tl-Te the height of the second peak in the theoretical curves is very sensitive to small increases ($\sim$1%) in ω_{13}/RT (or v_{13}/RT) beyond the values listed in the Tables, indicating the tendency for phase separation. For the values of ω_{13} (and v_{13}), given in the Table, the height of the second peak (not shown in the diagram) is about unity.

It is well known in the theory of binary regular or conformal solutions [see, for example, Guggenheim (1952), Longuet-Higgins (1951)] that the concentration dependences of G_M, and of the heat (H_M) and entropy (S_M) of mixing can in general be simultaneously fitted with the experimental data only if the interaction parameter is assumed to be temperature dependent. In the same spirit in our work we have to assume that g and ω_{ij} (or v_{ij}) are temperature dependent as we have done in deriving expressions (5.16) and (5.28) for H_M. If the temperature dependence of g and ω_{ij} (or v_{ij}) is ignored then H_M and S_M are readily calculated using the values of n_3 [and consequently of n_1 and n_2 from Eqn. (5.1)] given in Figs. 5.1(a-d) and the values of g etc. from Table 5.1. One finds that for Tl-Te, the values of H_M so calculated agree with experiment to within 5% over the whole concentration range, while the deviations

for S_M are considerably larger. In particular at the chemical composition c = 2/3, the calculated $S_M \simeq 0$, while the observed S_M is negative. In contrast, for Cu-Sn system both H_M and S_M so calculated are considerably in error with experiment. The relative importance of the terms involving the temperature derivatives of g and ω_{ij} (or v_{ij}) in the expressions for H_M and S_M would of course vary from system to system, and the above comments are made here only to illustrate that the parameters g etc. should be determined from the observed values of G_M rather than of H_M.

As an illustration of the extent to which agreement can be obtained for H_M and S_M, we give plots of H_M and S_M for Tl-Te (Fig. 5.4), in which the theoretical curves were calculated by taking $dg/dT = -0.44\,R$, and

$$d\omega_{13}/dT = -1.2R \quad , \qquad \text{for approximation (a)}$$

and

$$dv_{23}/dT = 0.7R \; , \quad dv_{13}/dT = -R \; , \; \text{for approximation (b)} \; .$$

(5.48)

The temperature dependence of the parameters not listed was taken to be zero. The fact that H_M is concave for $c < c_c$ and convex for $c > c_c$ is connected with the fact that ω_{23} (v_{23}) and ω_{13} (v_{13}) are of opposite signs for

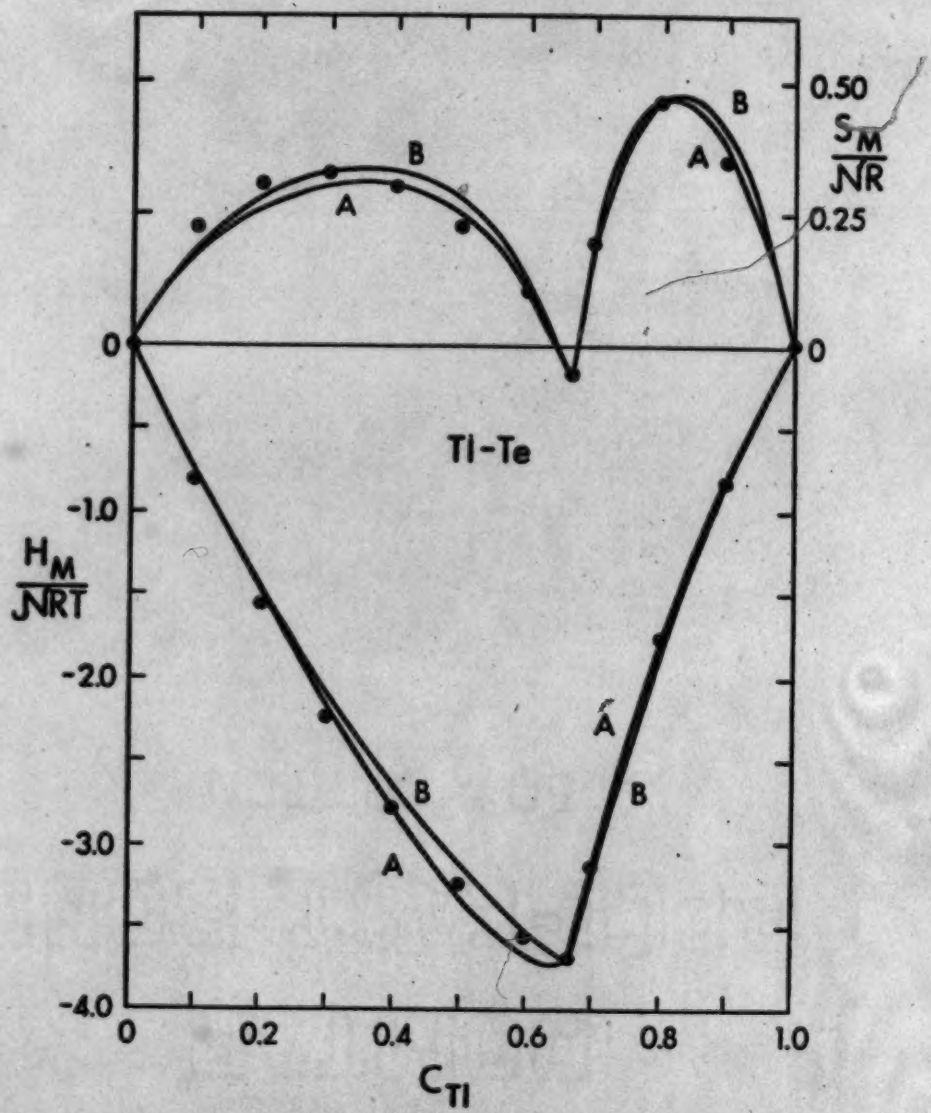

Fig. 5.4. Heat and entropy of mixing for Tl-Te system. Theoretical curves A: conformal solution approximation and B: Flory's approximation - see text. • Experimental data from Nakamura and Shimoji (1971).

this system. Note also the signs of their temperature derivatives given in Eqn. (5.48).

5.6 Discussion and Concluding Remarks

We observe from Figs. 5.1(a-d), that both the approximations (a) and (b) reproduce the observed concentration dependence of the free energy of mixing G_M remarkably well for the systems examined. The activities and S_{CC} which depend respectively on the first and second derivatives of G_M with respect to concentration provide more sensitive tests for the model. As seen from Figs. 5.2 and 5.3, the agreement with experiment for these quantities also is not unsatisfactory. For the Tl-Te and Mg-Bi systems for which ω_{12} and v_{12} were set equal to zero, the theoretical values of the activities a_{Tl} and a_{Mg} can be somewhat adjusted in the concentration range $0 < c < c_c$ by taking a non-zero ω_{12} and v_{12} [see Eqns. (5.23) and (5.29)], but this does not seem to improve the overall fit with experiment.

As regards the values of the interaction parameters required to fit the experimental data it is gratifying to see that for each of the systems examined, the two approximations yield for the (free) energy g of formation of chemical complexes values

which are within 20% of each other. Also, in each case, $\omega_{12} \simeq v_{12}$. However, the values of ω_{23} and ω_{13} differ in some cases substantially from the corresponding v_{23} and v_{13}. This is probably related to the differences in the definitions of ω_{ij} and v_{ij} which are likely to be significant when the chemical complex is involved, i.e. for (ij) = 2,3 and 1,3. The tracing of relations between ω and v, however, must await their interpretation in terms of the basic interatomic interactions between the A and B atoms. We should also recall that the use of the expressions (5.7) and (5.10) for G' entails the assumption that the interactions ω_{ij} and v_{ij} are small quantities - for binary regular solutions one usually considers the expression corresponding to (5.7) to be approximately valid for $|\omega_{12}| < 2RT$ (see §3.4). In Table 5.1, some of $|\omega_{23}|$ etc. are as large as 4RT. It is possible that these large values of ω_{ij} (or v_{ij}) needed to fit the data are partly reflecting the inadequacy of the approximations in which the combinatorial terms in (5.7) and (5.10) are treated. In this connection it is interesting to note that for the Mg-Bi system v_{23} and v_{13} are considerably smaller than ω_{23} and ω_{13}, so that for this system the approximation (b) is to be preferred over the approximation (a). This is not surprising in view

of the discussion of the two approximations given §5.2 and §5.4 - in Mg-Bi there is a strong tendency to form chemical complexes and $\mu+\nu$ (=5) is relatively large.

In conclusion, it has been shown in this chapter, by four examples, that for some compound forming binary molten systems the concentration dependence of the various thermodynamic quantities may be interpreted by assuming the formation of appropriate chemical complexes. The model then provides information on the free energy of formation of the chemical complexes $A_\mu B_\nu$ and on the interaction energies between the three species A, B and $A_\mu B_\nu$ in the solution. It will be realised that the model is a phenomenological one in which the concentration n_3 of the chemical complexes occurs as an order parameter. It is not possible to explicitly demonstrate the existence of these chemical complexes from the thermodynamic data or from the zero wave number ($q \to 0$) limit of the structure factors $S_{CC}(q)$ etc. However, if the chemical complexes are actually formed, then their equilibrium number and the geometric arrangements of the atoms in them should, in principle, be determinable from the knowledge of the structure factors at higher q values, just as the S(q) at higher q values reflects the molecular nature of a polyatomic fluid [Egelstaff et. al. (1971), Gubbins et. al. (1973)].

Finally, it is worth noting that the assumption of the formation of chemical complexes underlies, also, some of the recent discussions of the concentration dependence of the electron transport properties of Mg-Bi and Tl-Te systems [Enderby and Simmons (1969), Enderby and Collings (1970), Cutler (1971)]. In such discussions, of course, one has to make additional assumptions regarding the behaviour of the valence electrons on formation of the chemical complexes. In as much as the present work describes the concentration dependence of the thermodynamic properties quantitatively and, additionally, allows one to infer the number of chemical complexes at any given temperature and pressure from the thermodynamic data, it may be helpful towards a more quantitative interpretation of the transport properties of these systems.

CHAPTER 6

THE STRUCTURE FACTORS FOR ARBITRARY q INTERACTING BINARY MIXTURES

6.1 Introduction

The work of the last three chapters shows that the concentration dependence of the long wavelength (wave number $q \to 0$) limit of the structure factors exhibit widely varying features depending on the type of molten system under consideration. In particular, we saw that the deviation of the concentration fluctuations $S_{CC}(0)$ from the ideal value (c_1c_2) reflects rather sensitively the nature of the interatomic interactions in the mixture. On the other hand, as discussed in §2.2, the sum rule obeyed by a structure factor and its short wavelength $(q \to \infty)$ limit are the same for every system - for example, $a_{ij}(q)$ and $S_{CC}(q)$ respectively obey the sum rules (2.22) and (2.21) and $a_{ij}(\infty) = 1$ and $S_{CC}(\infty) = c_1c_2$. Thus we expect that the structure factors at intermediate q also depend, in general, on the interatomic interactions in the mixture. We may recall, parenthetically, that the knowledge of the structure factors at non-zero q is crucial, not only for understanding the usual X-ray and neutron scattering experiments in a mixture, but also calculating the electron transport properties of alloys of metals.

The calculation of the structure factors for arbitrary q is far from easy and, in fact, the only calculations available to date seem to be for a mixture of hard spheres using Percus-Yevick approximation [Lebowitz (1964), Ashcroft and Langreth (1967), Enderby and North (1968)]. Here, as the name implies, one regards the system as a random mixture of hard spheres of appropriate atomic (molecular) diameters, so that the distribution of the two types of atoms (molecules) is entirely governed by their sizes. The model clearly corresponds to an athermal type mixture of Chapter 3 [$\omega = 0$ in Eqns. (3.25) and (3.42)].† It thus cannot be

---

† It is to be noted that even within the framework of the model, the derivation of the expression (3.42) for G_M and hence (3.44) for $S_{CC}(0)$, on the one hand, and of the expressions for the various structure factors $S_{CC}(q)$ etc. on the other, involve other mathematical approximations. Hence, for example, the value of $\lim_{q\to 0} S_{CC}(q)$ from the latter calculations would, in general, not agree with the expression (3.44) [with $\omega = 0$] for $S_{CC}(0)$. If, however, $\sigma_1/\sigma_2 = (V_1^{(o)}/V_2^{(o)})^{1/3} \simeq 1$, both give $S_{CC}(0) = c(1-c)$. For this case $S_{CC}(q) = c(1-c)$ for all q and $S_{NC}(q) \equiv 0$, and we have a substitutional alloy at all q.

expected to give agreement with experiment at $q \to 0$ limit even for the simplest of real systems. For example, for Na-K alloy, with $(\sigma_K/\sigma_{Na})^3 \simeq (V_K^{(o)}/V_{Na}^{(o)}) \simeq 2$ (σ_K, σ_{Na}, diameters of K and Na atoms respectively), the hard sphere model gives, at $c = 1/2$, $S_{CC}(0) \simeq 0.24$, whereas the experimental value, at 100°C, is $S_{CC}(0) \simeq 0.55$ (see Fig.3.4).

The purpose of the present chapter is to present an approximate modification of the hard sphere treatment so that the $q \to 0$ limit of $S_{CC}(q)$ is more in accord with that for a weakly interacting system - rather than for an athermal or non-interacting mixture - and then to examine, by an example, the behaviour of the structure factors at non-zero q on the basis of this approximation. The basic equations are collected together in §6.2 and the modification of the hard sphere model is described in §6.3. Section 6.4 gives the numerical example and is followed by a brief discussion of the results and their significance (§6.5).

6.2 Basic Equations

6.2.1 Direct Correlation Functions and Structure Factors

There are essentially two approaches to the calculation of the pair correlation function g(r) of a liquid (or of $g_{ij}(r)$ for a mixture). The first, developed variously by Bogoliubov, Born and Green, Yvon, and Kirkwood [for a review and references see, for example, Cole (1967)] results in a heirarchy of differentio-

integral equations which express the pair correlation function in terms of the interatomic potentials and the triplet correlation functions $g^{(3)}$, the triplet in terms of quadruplet and so on. In actual calculations one truncates these BBGYK equations at the first by making some convenient approximation for the triplet correlation functions $g^{(3)}$, such as the super-position or convolution approximations. The second approach involves instead the substitution of an approximate expression for the direct correlation function, first introduced by Ornstein and Zernike. Of several approximations available, the Percus-Yevick (PY) theory [Percus and Yevick (1958)] has proved most convenient and we base our calculations on it.

For a binary system, the direct correlation functions $C_{ij}(r) = C_{ji}(r)$, $i,j = 1,2$, are defined by the relations

$$h_{ij}(r) = C_{ij}(r) + n \sum_{\ell=1}^{2} c_\ell \int h_{i\ell}(r') C_{\ell j}(|r-r'|) d^3r' \qquad (6.1)$$

where n is the number density, c_ℓ is the concentration of atoms of type ℓ ($\ell = 1,2$) and

$$h_{ij}(r) = g_{ij}(r) - 1 . \qquad (6.2)$$

Denoting the Fourier transform of $h_{ij}(r)$ by $h_{ij}(q)$

$$h_{ij}(q) = \int h_{ij}(r) e^{i\vec{q}\cdot\vec{r}}\, d^3r \quad , \tag{6.3}$$

and similarly the Fourier transform of $C_{ij}(r)$ by $C_{ij}(q)$, one obtains from (6.1)

$$h_{ij}(q) = C_{ij}(q) + n \sum_{\ell=1}^{2} c_\ell h_{i\ell}(q) C_{\ell j}(q) . \tag{6.4}$$

Remembering the definition of the Faber-Ziman structure factors $a_{ij}(q)$, Eqn. (2.1), one has

$$\begin{aligned} a_{ij}(q) &= 1 + n\int [g_{ij}(r) - 1] e^{i\vec{q}\cdot\vec{r}}\, d^3r \\ &= 1 + n h_{ij}(q) \quad . \end{aligned} \tag{6.5}$$

Hence, from (6.4) and (6.5),

$$\begin{aligned} a_{11}(q) &= D^{-1}(q)\,[1 + nc_2(C_{11}(q) - C_{22}(q)) \\ &\quad - n^2 c_2^2 (C_{11}(q)C_{22}(q) - C_{12}^2(q))] \\ a_{22}(q) &= D^{-1}(q)\,[1 + nc_1(C_{22}(q) - C_{11}(q)) \\ &\quad - n^2 c_1^2 (C_{11}(q)C_{22}(q) - C_{12}^2(q))] \\ a_{12} &= D^{-1}(q)\,[1 - n(c_1 C_{11}(q) + c_2 C_{22}(q) - C_{12}(q)) \\ &\quad + n^2 c_1 c_2 (C_{11}(q)C_{22}(q) - C_{12}^2(q))] \end{aligned} \tag{6.6}$$

where

$$D(q) = 1 - n(c_1 C_{11}(q) + c_2 C_{22}(q)) + n^2 c_1 c_2 (C_{11}(q)C_{22}(q) - C_{12}^2(q)) . \tag{6.7}$$

For a single component system the Eqns. (6.1), (6.4) and (6.6), of course, take the well known simple forms

$$h(r) = C(r) + n\int h(r')C(|r-r'|)d^3r'$$

$$h(q) = C(q) + nh(q)C(q)$$

and

$$a(q) \equiv S(q) = \frac{1}{1 - nC(q)} \quad . \tag{6.8}$$

The expressions for the number-concentration structure factors $S_{NN}(q)$ etc. for the binary mixture in terms of $C_{ij}(q)$ are readily written by substituting (6.6) into (2.17). In the following it will be convenient to work with the concentration fluctuation structure factor $S_{CC}(q)$ and the combinations

$$\theta(q) = S_{NN}(q) - [S_{NC}(q)/S_{CC}(q)]^2 S_{CC}(q) \tag{6.9}$$

and

$$\Delta(q) = -S_{NC}(q)/S_{CC}(q) \quad . \tag{6.10}$$

We observe from (2.32) and (2.33) that $\theta(q)$ and $\Delta(q)$ are defined such that

$$\theta(0) \equiv \theta = (\frac{NV}{V}) k_B T \kappa_T$$

and $\Delta(0) = \delta$, the dilatation factor. Substituting (6.6) into (2.17), one obtains

$$\theta(q) = \frac{1}{1-n(c_1^2 C_{11}(q)+c_2^2 C_{22}(q)+2c_1 c_2 C_{12}(q))} \tag{6.11}$$

$$\Delta(q) = n\theta(q)\,[c_1(C_{11}(q)-C_{12}(q))-c_2(C_{22}(q)-C_{12}(q))] \qquad (6.12)$$

and

$$S_{CC}(q)=\frac{c_1c_2[1-n(c_1^2C_{11}(q)+c_2^2C_{22}(q)+2c_1c_2C_{12}(q))]}{1-n(c_1C_{11}(q)+c_2C_{22}(q))+n^2c_1c_2(C_{11}(q)C_{22}(q)-C_{12}^2(q))} \qquad (6.13)$$

On using (6.11) and (6.12), $S_{CC}(q)$ can also be written in the form

$$S_{CC}(q) = \frac{c_1c_2}{1- nc_1c_2(C_{11}(q)+C_{22}(q)-2C_{12}(q))- c_1c_2\,\frac{\Delta^2(q)}{\theta(q)}}\,, \qquad (6.14)$$

which will be found useful later.

6.2.2 P-Y Approximation and Hard Sphere Model

In the P-Y approximation for a mixture, the interatomic potentials $\phi_{ij}(r)$ are related to $C_{ij}(r)$ by the relations [Percus (1962), Lebowitz (1964)]

$$g_{ij}(r)(e^{-\beta\phi_{ij}(r)} - 1) = C_{ij}(r)e^{-\beta\phi_{ij}(r)} \qquad (6.15)$$

where $\beta = 1/k_BT$. Equations (6.15) together with (6.1) and (6.2) are sufficient to determine $C_{ij}(r)$ or $g_{ij}(r)$ if $\phi_{ij}(r)$ are known.

For a mixture of hard spheres of diameters σ_1 and σ_2, one has

$$\begin{aligned} e^{-\beta\phi_{ij}} &= 0 \qquad \text{for} \quad r < \tfrac{1}{2}(\sigma_i+\sigma_j) \\ &= 1 \qquad \text{for} \quad r > \tfrac{1}{2}(\sigma_i+\sigma_j) \end{aligned} \qquad (6.16)$$

which imply, from (6.15), that

$$g_{ij}(r) = 0 \quad \text{for} \quad r < \tfrac{1}{2}(\sigma_i+\sigma_j)$$

and

$$C_{ij}(r) = 0 \quad \text{for} \quad r > \tfrac{1}{2}(\sigma_i+\sigma_j) \ . \qquad (6.17)$$

With (6.17), the solution of the Eqn. (6.1) for $C_{ij}(r)$ is [Lebowitz (1964)] ($x \equiv r-\lambda$)

$$-C_{ii}(r) = a_i + b_i r + dr^3 \qquad r < \sigma_i \ , \quad i=1,2$$

$$-C_{12}(r) = a_1 \ , \quad r < \lambda \ , \qquad \lambda = \tfrac{1}{2}(\sigma_2-\sigma_1)$$

$$= a_1 + [bx^2 + 4\lambda dx^3 + dx^4]/r \ , \quad \lambda \le r \le \tfrac{1}{2}(\sigma_1+\sigma_2)$$

(6.18)

where we have assumed, for definiteness, that $\sigma_2 \ge \sigma_1$ and where a_i, b_i, a,b,d are constants which are functions of σ_1, σ_2, the number density n of the atoms and the concentration of two types of atoms. For brevity they will not be written here explicitly. When $\sigma_1 = \sigma_2$, the various constants are independent of concentration and $a_1 = a_2$, $b_1 = b_2 = b$, so that[†]

$$C_{11}(r) = C_{22}(r) = C_{12}(r), \quad \text{for} \quad \sigma_1 = \sigma_2 \ .$$

[†] As to be expected, each $C_{ij}(r)$ is then just C(r) of a one component hard sphere fluid, the expression for which was first obtained by Wertheim (1963) and Thiele (1963).

Remembering the relations between the Fourier transforms $C_{ij}(q)$ of $C_{ij}(r)$ and the various structure factors, one sees that for hard sphere mixture of equal diameters

$$S_{CC}(q) = c_1 c_2 , \qquad \Delta(q) = 0$$

and $$a_{11}(q) = a_{22}(q) = a_{12}(q)$$

so that one has a simple substitutional mixture.

The calculation $C_{ij}(q)$ from (6.18) for any σ_1 and σ_2, involves integrals of the type $\int \sin qr\, r^n dr$ with $n = 0,2,\ldots,4$, which can be evaluated in closed form. The resulting expressions for $C_{ij}(q)$ and hence the structure factors have been obtained by Ashcroft and Langreth (1967) and Enderby and North (1968). Since they are lengthy we shall not reproduce them here.

6.3 A Modification of the Hard Sphere Model

The interatomic potential consists of a strong short range repulsive interaction and a relatively long range weak attractive interaction (see Fig. 6.1). The hard sphere model takes into account the former in the form of an infinitely strong repulsive core but neglects the attractive interaction. An approximate

method[†] of taking the latter into account is suggested by the following argument.

We notice from (6.15) that if $\phi_{ij}(r) = 0$, at a given r, then provided $g_{ij}(r)$ is non singular, $C_{ij}(r) = 0$. Further if $C_{ij}(r)$ are zero for all r, then eqn. (6.1) gives $g_{ij}(r) = 1$ for all r [ideal gas or hard sphere model of zero diameter!]. This suggests that if $|\beta\phi_{ij}(r)| << 1$, we can set, approximately, in (6.15) $g_{ij}(r) \simeq 1$ and thus obtain

$$C_{ij}(r) \simeq -\beta\phi_{ij}(r), \quad |\phi_{ij}(r)| << \frac{1}{\beta} \ . \qquad (6.19)$$

In analogy with the case of one component system, this approximation may be referred to as the random phase

---

[†] The method is an extension of that proposed by Woodhead-Galloway et.al. (1968) for a pure fluid. While this work was in progress it was pointed out to us by Professor March that a similar extension has been suggested by Woodhead-Galloway and Gaskell (1968). Our procedure of specifying the repulsive core and the attractive potential (see below) differs however from that used in these works and the discussion of $S_{CC}(q)$ etc. presented here has not been given previously.

approximation (RPA) for the mixture.† Because $\phi_{ij}(r)$ is not small for small interatomic separation, the RPA is actually quite a poor approximation for liquid media. To take into account both the strong short range repulsive interaction and the weak long range attractive interaction, we assume that $C_{ij}(r)$ has the form

$$C_{ij}(r) \simeq C_{ij}^{HS}(r) - \beta\chi_{ij}(r) \tag{6.20}$$

where $C_{ij}^{HS}(r)$ are the direct correlation functions for the mixture of hard spheres of appropriate (see below) diameters σ_1 and σ_2 and

---

† For a pure fluid, the Fourier transform of the exact Born-Green-Yvon equation connecting $g(r)$ to $\phi(r)$ and the triplet correlation function is ($q \neq 0$) - [see, e.g. Brout (1965)]

$$\langle \rho_q \rho_{-q} \rangle = N + \frac{\beta}{N} \sum_k \phi_k \frac{k.q}{q^2} \langle \rho_k \rho_q \rho_{-k-q} \rangle \tag{6.19}'$$

where $\rho_q = \sum_{j=1}^{N} e^{i\vec{q}.\vec{R}_j}$, R_j being the position of the j^{th} atom. The RPA corresponds to neglecting all terms in the sum in (6.19)' except $k = -q$, whence

$$S(q) = \frac{1}{N} \langle \rho_q \rho_{-q} \rangle = [1 + \beta n \phi_q]^{-1} \tag{6.19}''$$

which implies, comparing (6.8), $C(q) = -\beta n \phi_q$.

$$\chi_{ij}(r) = \phi_{ij}(r) \quad \text{for} \quad r \geq r_{ij}^m \geq \tfrac{1}{2}(\sigma_i+\sigma_j) \tag{6.21}$$

$$= \phi_{ij}(r_j^m) \quad \text{for} \quad r \leq r_{ij}^m \tag{6.22}$$

where r_{ij}^m is the position at which $\phi_{ij}(r)$ is minimum. The approximation (6.21) implies that beyond r_{ij}^m, the potential can be considered to be weak, since use of (6.21) in (6.20) gives

$$C_{ij}(r) \simeq -\beta\phi_{ij}(r), \quad r \geq r_{ij}^m \tag{6.23}$$

as in RPA.

The choice of a non-zero $\chi_{ij}(r)$, for $r < r_{ij}^m$, needs some comment. First, if $\chi_{ij}(r)$ is set equal to zero for $r < r_{ij}^m$, then this abrupt cut off gives rise to spurious harmonics in $C_{ij}(q)$ and hence in various structure factors. Secondly, as discussed by Gaskell (1970) for a pure fluid, a non-zero $\chi_{ij}(r)$ in the core region is necessary to satisfy the physical requirements that the pair distribution functions $g_{ij}(r)$ (calculated from 6.20-6.22) be zero for $r < \frac{1}{2}(\sigma_i+\sigma_j)$. To find such a $\chi_{ij}(r)$ is a difficult mathematical problem and Gaskell in his work on argon also took $\chi(r)$ to be a constant, say χ_o, inside the core region. He adjusted the value of χ_o so that the average of $g(r)$ over the core is zero, i.e. $\int_0^\sigma g(r)dr = 0$. This gives for argon at 86.5°K, $\beta\chi_o = -1.67$ compared to the value of $\beta\chi_o = -1.39$ from (6.22). Our suggestion for $\chi(r)$ has, perhaps, the

advantage that it requires no additional work to determine χ_o and that it [our $\chi(r)$] is smooth over the whole range of r. We note parenthetically that in Gaskell's work, $\chi(r) = \phi(r)$ for $r \geq r_o$ and $\chi(r) = \chi_o$ for $r \leq r_o$ where r_o $(= \sigma)$ is the value of r at which $\phi(r) = 0$.

6.4 Numerical Calculations

6.4.1 Calculations for Liquid Argon

Before presenting calculations for a mixture, it is useful to consider the application of the above approximation to a pure liquid. We choose liquid argon, for which the interatomic potential is usually given in the Lennard-Jones form:

$$\phi(r) = 4\varepsilon\left[\left(\frac{r_o}{r}\right)^{12} - \left(\frac{r_o}{r}\right)^{6}\right] \quad . \tag{6.24}$$

For argon,

$$\frac{\varepsilon}{k_B} = 123°K \ , \qquad r_o = 3.4 \times 10^{-8} \text{ cm} \ . \tag{6.25}$$

We make the calculation at 85°K at which molar volume is 28.34 cm and $n = 2.14 \times 10^{22}/\text{cm}^3$. The functions $\phi(r)$ and $\chi(r)$ are depicted in Fig. 6.1 $(r_m = 2^{1/6} r_o)$. One may physically expect the appropriate hard core diameter σ to be somewhat less than the value (r_o) at which the potential is zero. Although the fit for the structure factor, $S(q)$ $(= \theta(q))$

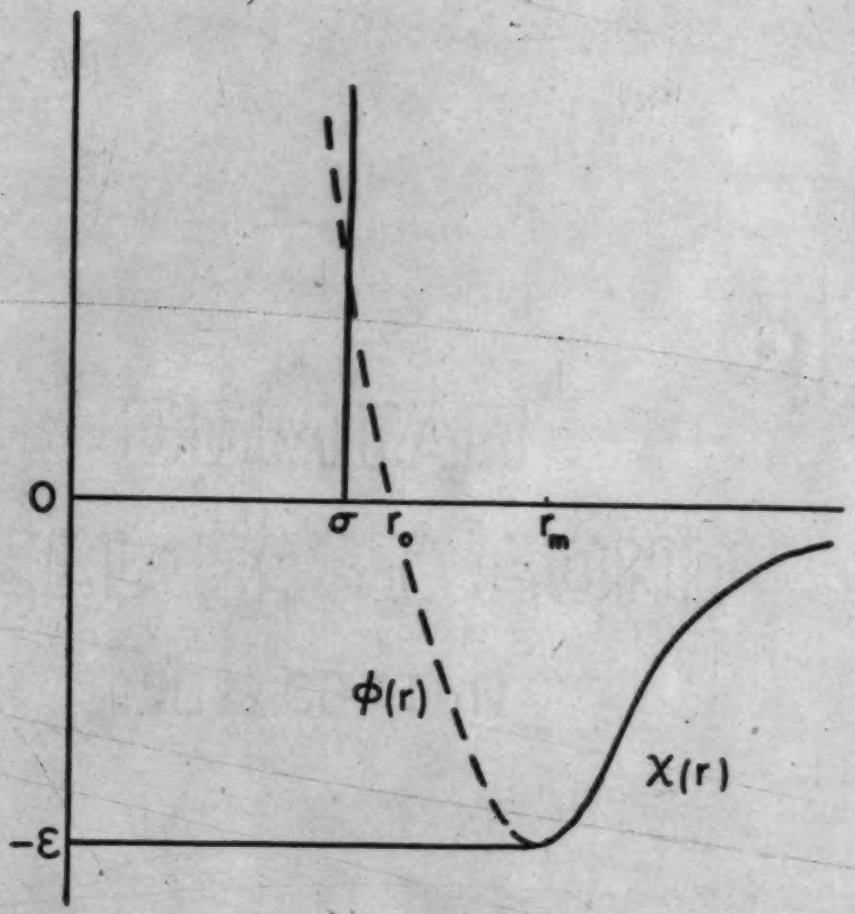

Fig. 6.1. Sketch of the model potential showing $\phi(r)$ of Lennard-Jones form and $\chi(r)$ as well as the hard core.

with experiment was not unreasonable for the choice $\sigma = r_o$, a somewhat better agreement with experiment is obtained for the choice $\sigma = 0.98\ r_o$. The theoretical and experimental results are shown in Fig. 6.2. We observe that the agreement with experiment is not unsatisfactory.

6.4.2 Mixture

To examine the effects of the long range attractive interactions on the various structure factors of a binary mixture, we shall here consider, for simplicity, a mixture in which $\phi_{11}(r)$, $\phi_{22}(r)$ and $\phi_{12}(r)$ have the form (6.24) with the same r_o, so that one may take, to a first approximation†, the hard core diameters for the two species to be equal ($\sigma_1 = \sigma_2 = \sigma$, say). Further, the three $\phi_{ij}(r)$ are then proportional to one another, and similarly the three $\chi_{ij}(r)$ and hence their Fourier transforms $\chi_{ij}(q)$. Denoting $\chi_{11}(q) \equiv \chi(q)$ and introducing two dimensionless parameters γ and $\mathcal{R}$:

$$\gamma = \frac{\varepsilon_{11} - \varepsilon_{12}}{\varepsilon_{11}} \quad , \quad 2\mathcal{R} = \frac{\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12}}{\varepsilon_{11}} \quad , \qquad (6.26)$$

to measure relative differences in the (minimum) depths of $\phi_{ij}(r)$, one has

---

† This may be expected to be reasonable if the differences in various ε_{ij} are small (see below).

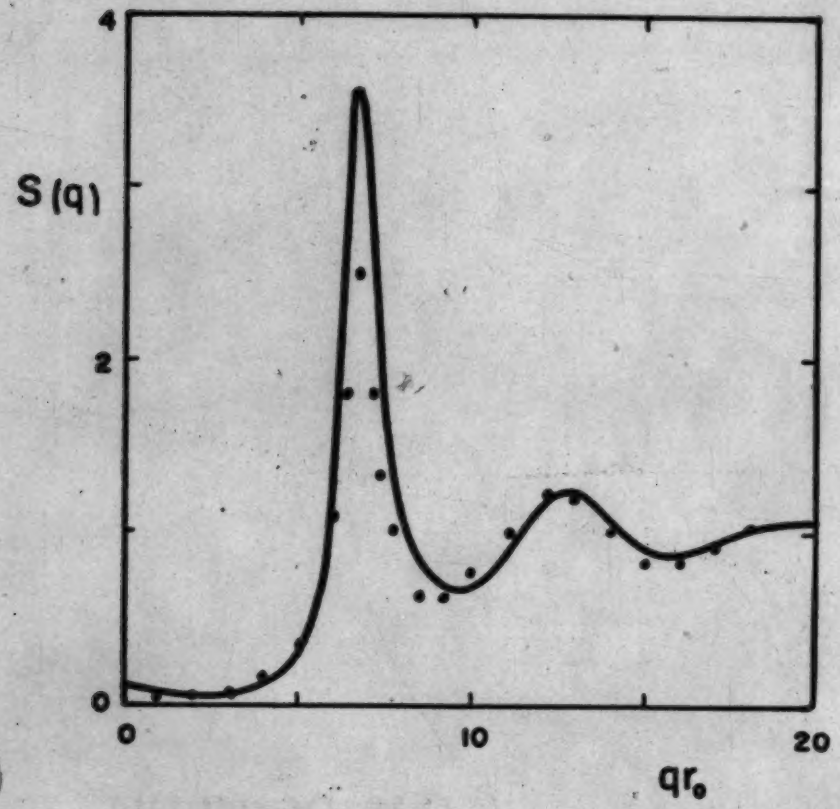

Fig. 6.2. Model S(q) (solid line) for $\epsilon/k_B = 123°K$, $r_o = 3.4\times10^{-8}$ cm and $\sigma = 0.98\ r_o$ compared with experimental S(q) for Ar at 85°K.

$$\chi_{11}(q) \equiv \chi(q) , \qquad \chi_{12}(q) = (1-\gamma)\chi(q)$$

and $$\chi_{22}(q) = (2\mathcal{R} - 2\gamma + 1)\chi(q) \quad . \tag{6.27}$$

Finally, recalling (6.20), one has

$$C_{ij}(q) = C_{HS}(q) - \beta\chi_{ij}(q) \tag{6.28}$$

where $C_{HS}(q)$ is the Fourier transform of the direct correlation function $C_{HS}(r)$ for a fluid of hard spheres of diameter σ.

Substituting (6.27) and (6.28) into the expressions (6.11), (6.12) and (6.14) for $\theta(q)$, $\Delta(q)$ and $S_{CC}(q)$, one obtains

$$\theta(q) = \frac{1}{1 - nC_{HS}(q) + n\beta\chi(q)[1 - 2\gamma c_2 + 2\mathcal{R}c_2^2]} \tag{6.29}$$

$$\Delta(q) = -n\theta(q)\chi(q)\beta(\gamma - 2\mathcal{R}c_2) \tag{6.30}$$

and

$$S_{CC}(q) = \frac{c_1 c_2}{1 + \beta(2n\chi(q)\mathcal{R})c_1c_2 - c_1c_2\frac{\Delta^2(q)}{\theta(q)}} \quad . \tag{6.31}$$

If $\varepsilon_{11} = \varepsilon_{22}$, then, from (6.26), $\gamma = \mathcal{R}$ and the expressions for $\theta(q)$ and $\Delta(q)$ take the form ($\gamma = \mathcal{R}$)

$$\theta(q) = \frac{1}{1 - nC_{HS}(q) + n\beta\chi(q)(1 - 2\mathcal{R}c_1c_2)} \tag{6.32}$$

$$\Delta(q) = -n\theta(q)\beta\chi(q)\mathcal{R}(1 - 2c_2) \quad . \tag{6.33}$$

We note that this case corresponds to systems where the volumes ($V_1^{(o)}$ and $V_2^{(o)}$) of the two pure species are equal. Indeed, the expression (6.33) for $\Delta(q)$ has the same concentration dependence as the expression (3.31) for δ ($\equiv \Delta(0)$) for a conformal solution, if in the latter one sets $V_1^{(o)} = V_2^{(o)}$. Finally, for a mixture which satisfies the substitutional bypothesis, $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{12}$ and hence $\gamma = \mathcal{A} = 0$, so that $\theta(q)$ is independent of concentration, $\Delta(q) = 0$ and $S_{CC}(q) = c_1 c_2$, as expected.

We observe from (6.33) that at $c = \frac{1}{2}$, $\Delta(q) = 0$, so that, for this case ($\mathcal{A} = \gamma$, $c_2 = \frac{1}{2}$), the value of $S_{CC}(q)$ depends on the single parameter

$$n\chi(q)\,\frac{\mathcal{A}}{k_B T} \equiv \frac{\omega(q)}{k_B T} \tag{6.34}$$

which defines $\omega(q)$. If we use the interatomic potential for liquid argon to calculate $\chi(q)$, we find for $\chi(0) \equiv \chi(q=0)$

$$\left(\frac{n}{k_B T}\right)\chi(0) = 4\pi\left(\frac{n}{k_B T}\right)\int_0^\infty \chi(r) r^2 dr$$

$$= -\left(\frac{32}{9}\right)\pi n r_m^3 \left(\frac{\varepsilon}{k_B T}\right) = -\frac{1624}{T} \quad , \tag{6.35}$$

and hence $\omega(0)/k_B T = -1624\,\mathcal{A}/T$. For mixture having this value of $\omega(0)$, $S_{CC}(0)$ would become infinitely large, $T = 85°K$ if $\mathcal{A} \simeq 0.105$. For $\mathcal{A} > 0.105$, $S_{CC}(0)$ would be negative which is not allowed since S_{CC} is non-negative

by definition. In other words, for $\mathcal{R} = 0.105$, the critical temperature of mixing is 85°K. Now it may be seen from eqns. (6.30) and (6.31) that if $|\mathcal{R}|$ and $|\gamma| << 1$ (or, of course, if $|n\beta\chi(0)| << 1$), i.e. if the differences in the pairwise interaction energies are small, then since $\theta(0) \sim 0.06$, the term involving Δ in the denominator of (6.31) can be ignored at all concentrations for calculating $S_{cc}(0)$, and hence (6.31) gives

$$S_{cc}(0) \simeq \frac{c_1 c_2}{1 + (\frac{2\omega(0)}{k_B T})\ c_1 c_2} \qquad (6.36)$$

which is just the expression for $S_{cc}(0)$ derived in Chapter 3 from the expression for the free energy of a regular solution (in the zeroth approximation) or a conformal solution. As remarked earlier (see p. 127) we cannot in general expect that the approximate methods for calculating the $S_{cc}(q)$ etc. for arbitrary q, would give for $S_{cc}(0)$ etc., the same expressions as derived from the appropriate statistical mechanical theories of mixtures described in Chapter 3. It is, therefore, not unencouraging that the method suggested here gives, at least for the case $V_1^{(o)}/V_2^{(o)} \simeq 1$, and $|\mathcal{R}|$ and $|\gamma| << 1$, an expression for $S_{cc}(q)$ which in the limit $q \to 0$ agrees with that derived from statistical mechanics for this case.

In Figs. 6.3-6.6, we present some results of numerical calculations to illustrate the variation of the different structure factors with wave number q. For definiteness, we took throughout for $\chi(r)$ and σ the values appropriate to liquid argon as given in §6.4.1 and assumed for the mixture that $\mathcal{R} = \gamma$.

The results in Figs. 6.3 (a and b) are for $\mathcal{R} = 0.10$ and at $T = 85°K$ which (for this value of $\mathcal{R}$) as discussed above is close to critical solution temperature of the mixture, so that $S_{CC}(0)$ is very large as $q \to 0$ for $c_1 = c_2 = \frac{1}{2}$. Fig. 6.3a shows $\theta(q)$, $S_{CC}(q)$ and $\Delta(q)$ for $c_2 = \frac{1}{2}$ and $c_2 = 0.2$. [$\Delta(q)$, in our examples, is zero at $c_2 = \frac{1}{2}$ and is in general quite small at other concentrations since we are considering here only the mixtures with $V_1^{(o)} \simeq V_2^{(o)}$.] Fig. 6.3b shows $a_{ij}(q)$ for the same two concentrations.

Fig. 6.4 gives similarly the results at an elevated temperature $T = \frac{3}{2} T_c$, using the same $\mathcal{R}$ namely $\mathcal{R} = 0.1$.

As will be clear from the definition of $\mathcal{R}$, a positive value of $\mathcal{R}$ implies that like atom pairs have lower energy than the unlike atom pairs. To illustrate the behaviour of the structure factors when unlike atom pairs are energetically preferred, Fig. 6.5 gives the model structure factors for $\mathcal{R} = -0.2$ at $T = 85°K$. As expected, $S_{CC}(q)$ for $q \to 0$,

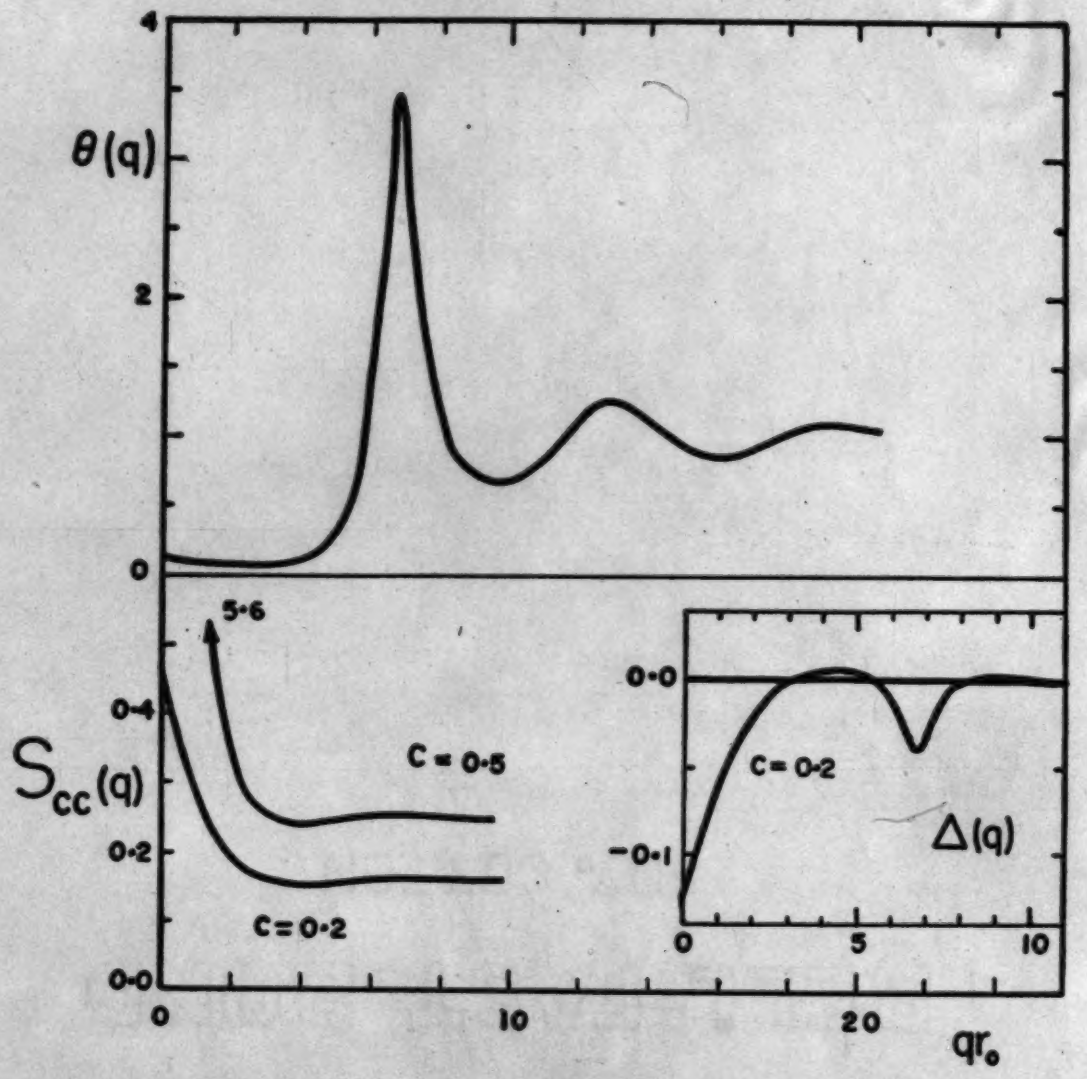

Fig. 6.3a. Model $\theta(q)$, $S_{CC}(q)$ and $\Delta(q)$ (inset) for two concentrations ($c = 1/2$, $c = 1/5$) taking $R = 0.10$, $T = 85^{\circ}$ (i.e. critical parameters).

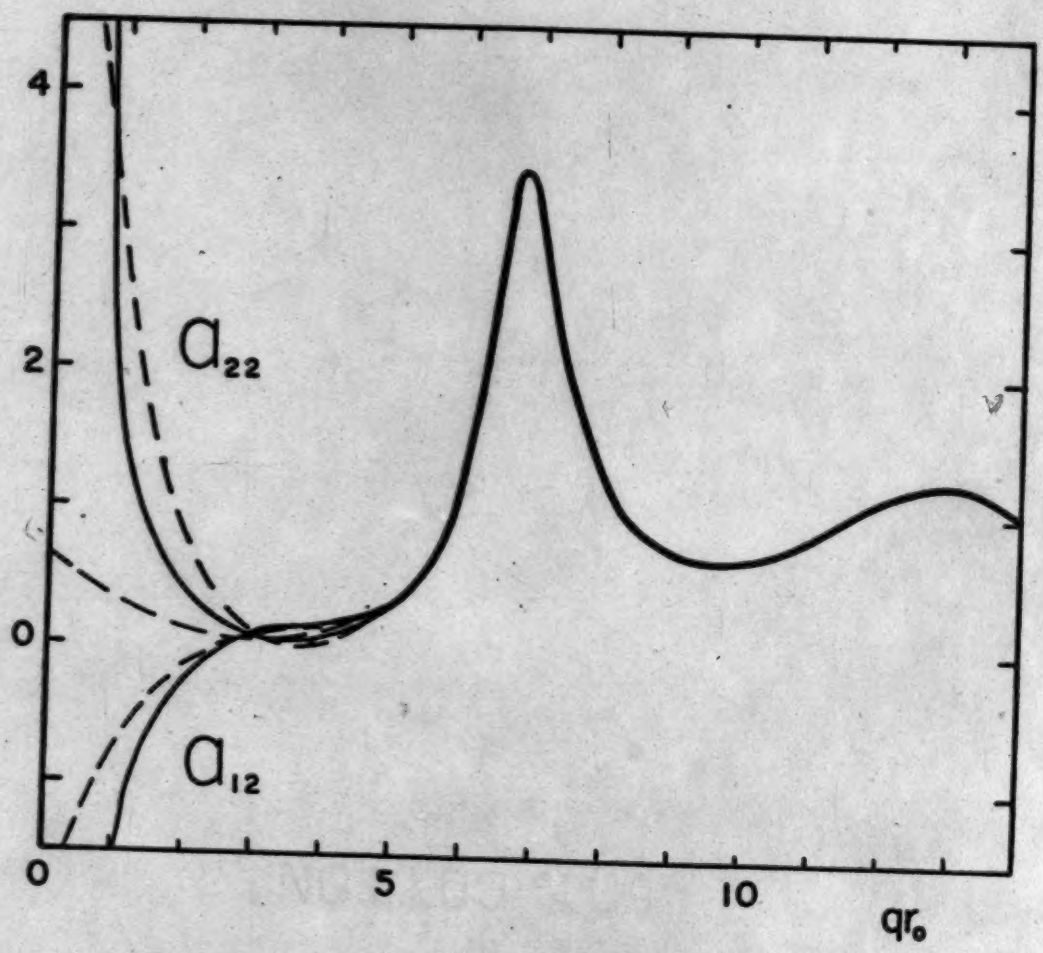

Fig. 6.3b. Model $a_{ij}(q)$ for the same parameters as Fig. 6.3a. ——— $c = 1/2$ $(a_{11} \equiv a_{22})$, – – – $c = 1/5$.

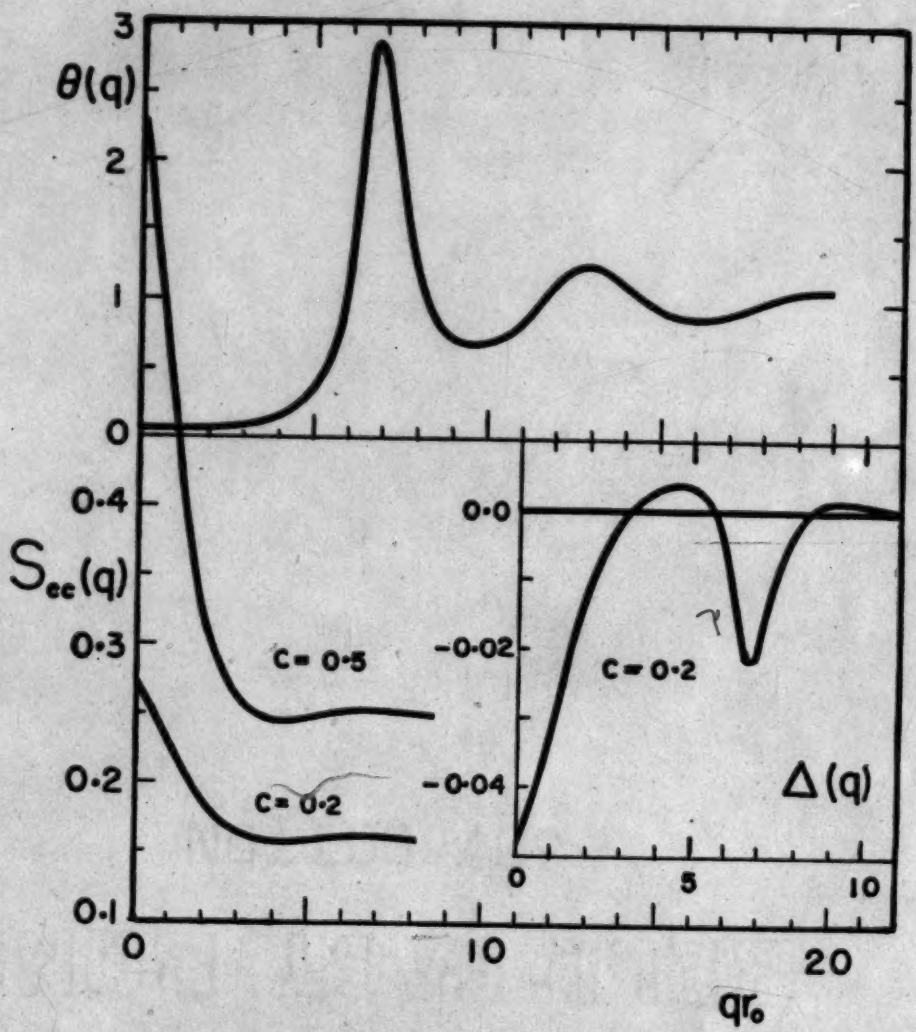

Fig. 6.4a. Model $\theta(q)$, $S_{CC}(q)$ and $\Delta(q)$ (inset) at an elevated temperature: $T = 3/2\ T_c$ with $R = 0.1$ ($T_c = 85°K$).

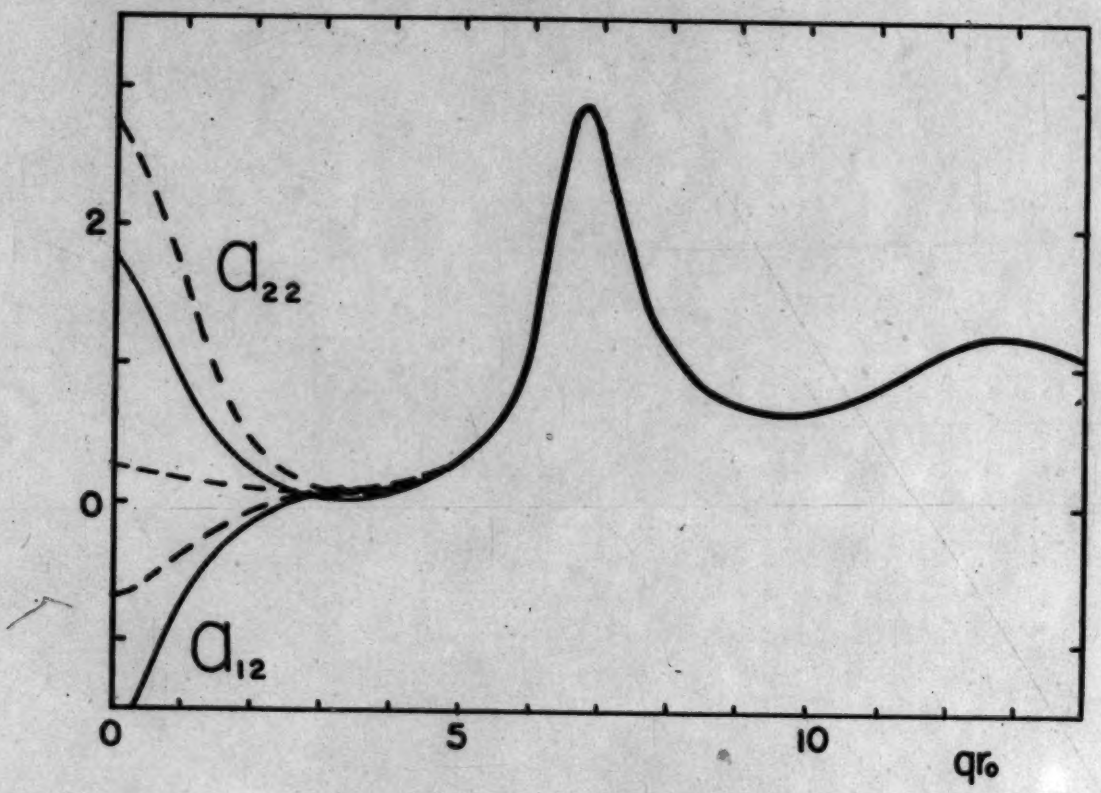

Fig. 6.4b. Model $a_{ij}(q)$ for the same parameters as Fig. 6.4a. ——— $c = 1/2$ $(a_{11} \equiv a_{22})$, – – – $c = 1/5$.

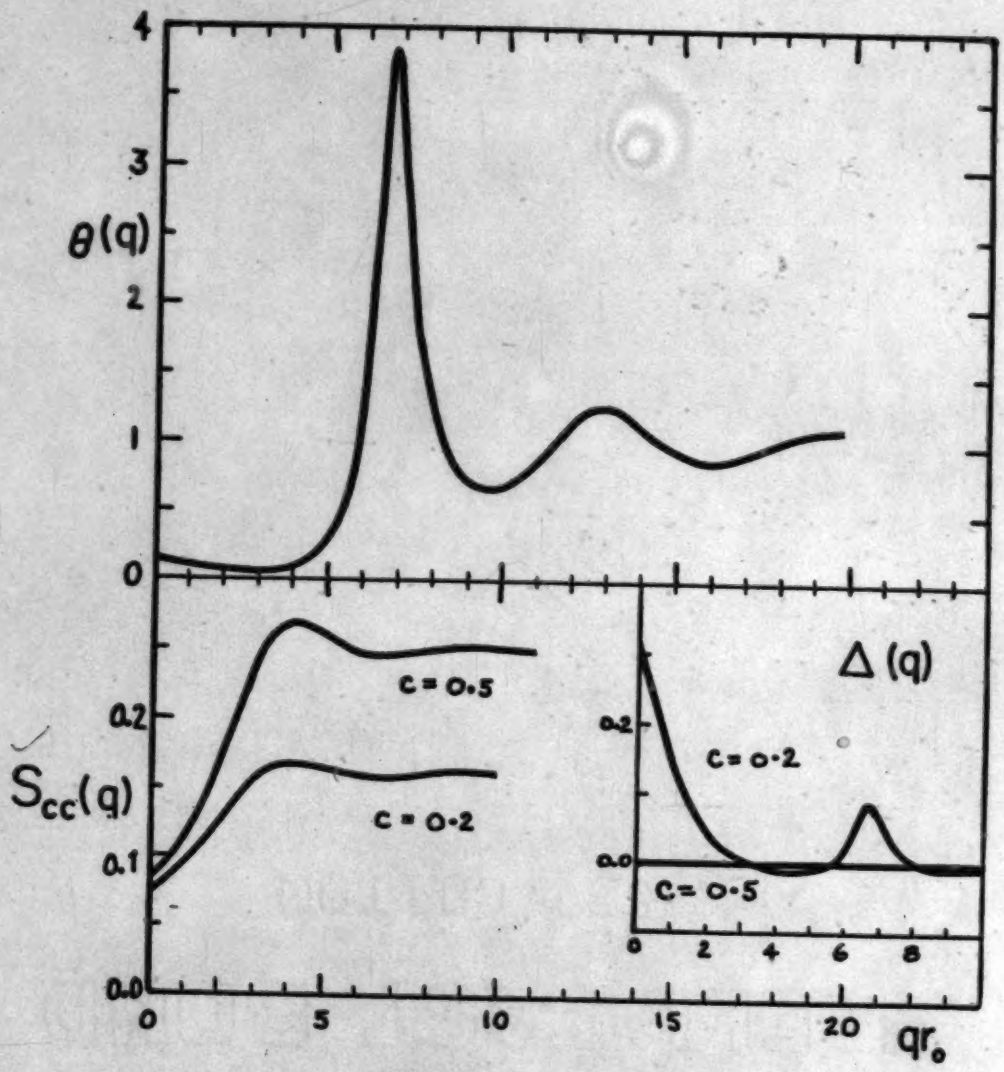

Fig. 6.5a. Model $\theta(q)$, $S_{CC}(q)$ and $\Delta(q)$ (inset) for $R = -0.2$, $T = 85°K$ for two concentrations.

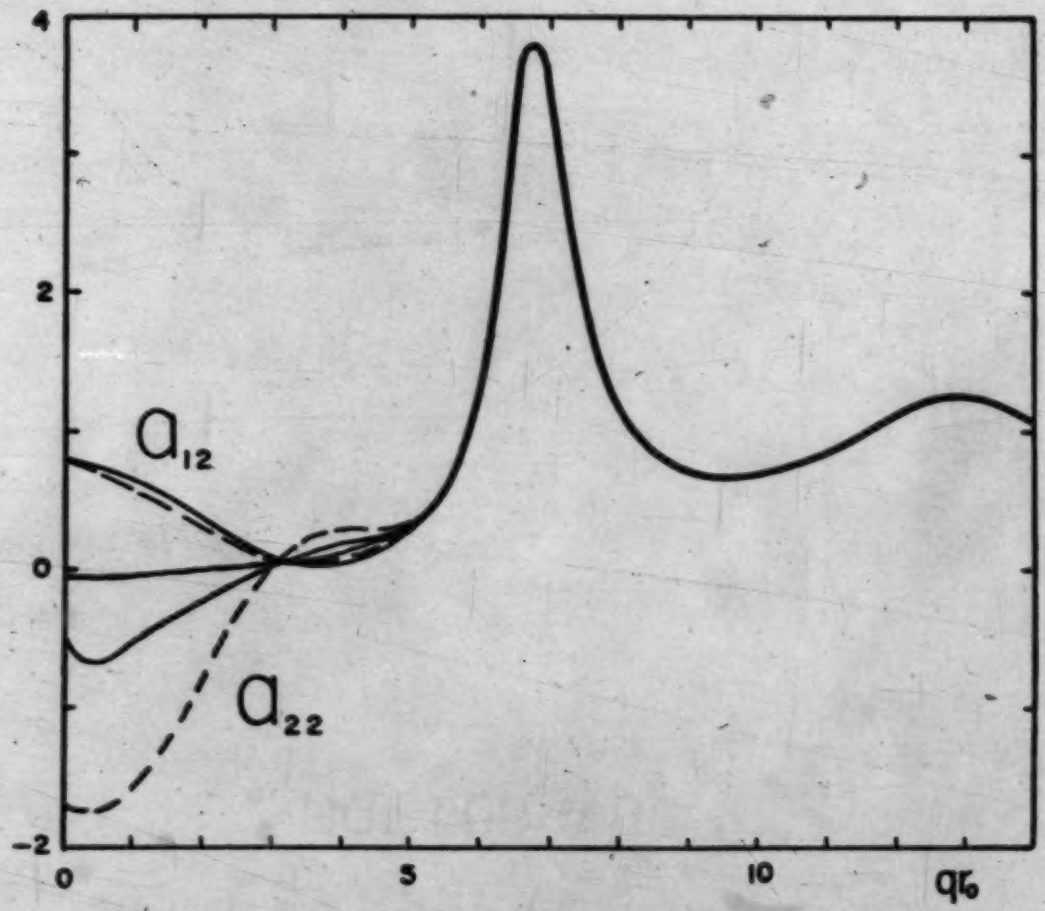

Fig. 6.5b. Model $a_{ij}(q)$ for the same parameters as Fig. 6.5a. ——— c = 1/2 ($a_{11} \equiv a_{22}$), – – – c = 1/5.

is now less than the ideal value (c_1c_2) in contrast to the case $\mathcal{R} > 0$. Also, it is found that the oscillations in $S_{CC}(q)$ damp less rapidly when $\mathcal{R} < 0$ than when $\mathcal{R} > 0$ (Fig. 6.6).

6.5 Discussion and Concluding Remarks

The major feature of the results depicted in Figs. 6.3-6.5 is that the effect of the difference in the interatomic potentials on the structure factors is primarily confined to the values of q in the range $0 < q \lesssim \frac{2}{3} q_o$, where q_o is the position of the main peak in $\theta(q)$ or $a_{ij}(q)$. For example, for q less than about $\frac{2}{3} q_o$, $S_{CC}(q)$ is quite different when $\mathcal{R} < 0$ from that when $\mathcal{R} > 0$, while beyond this q, $S_{CC}(q) \approx c_1c_2$, irrespective of the value $\mathcal{R}$. The partial structure factors $a_{ij}(q)$, for $q < \frac{2}{3} q_o$, are different from one another (except that $a_{11}(q) = a_{22}(q)$ for $c_2 = \frac{1}{2}$, since in our example $\Delta(q) = 0$ at this concentration) and depend on the concentration, the dependence of a_{ij} on both q and concentration being quite different when $\mathcal{R} < 0$ and when $\mathcal{R} > 0$. In contrast, for $q \gtrsim \frac{2}{3} q_o$, one has approximately $a_{11}(q) \approx a_{22}(q) \approx a_{12}(q)$ and the dependence on concentration is quite small. In other words, the $a_{ij}(q)$ here approximately obey the substitutional hypothesis.

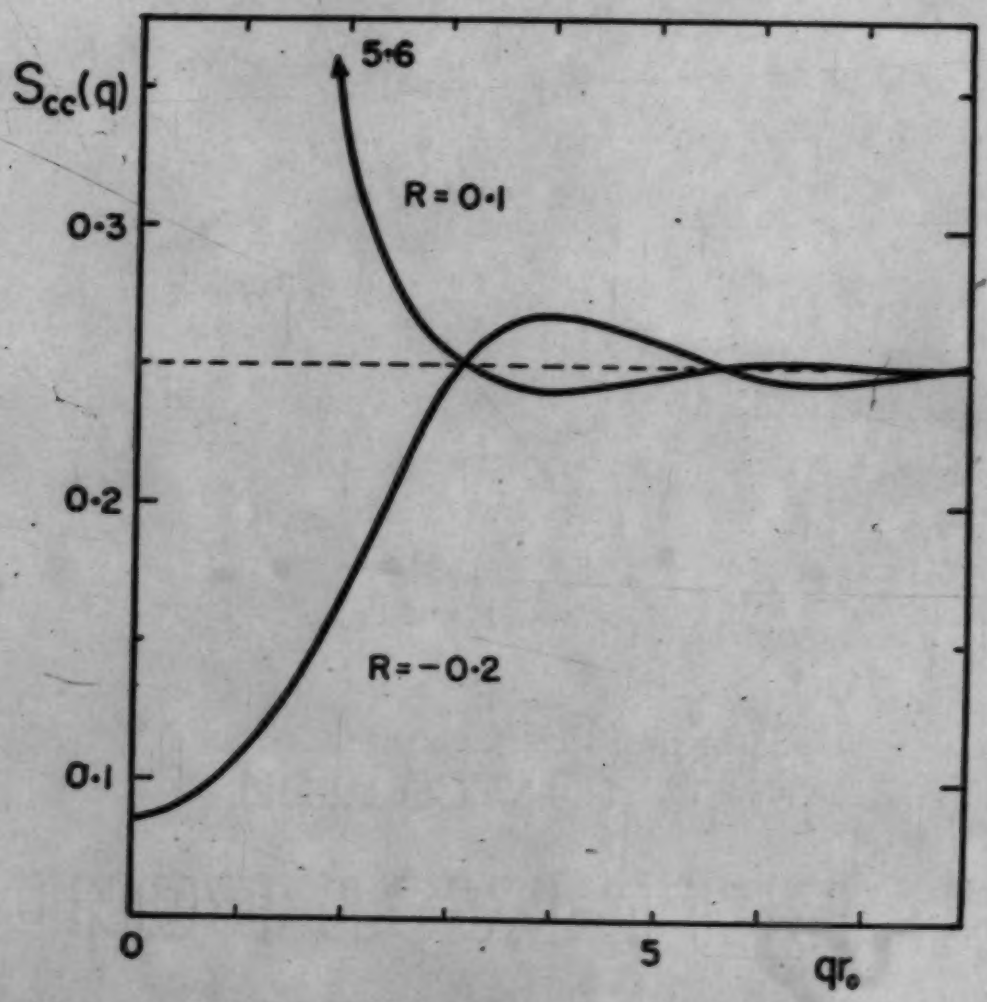

Fig. 6.6. $S_{CC}(q)$ for two values of R at T = 85°K.

In the calculations presented in Figs. 6.3-6.5, we have considered the mixtures with $V_1^{(o)} \simeq V_2^{(o)}$ so that the hard core diameters σ_i for the two types of atoms are equal. When the two diameters are not equal, one would still expect that the effects of the (weak) long range interactions are confined to q-values less than a value q_c where $q_c \simeq q_o$. For $q_c > q_o$ the structure factors may be expected to be approximately those given by the hard sphere approximation with different σ_i.

Our work thus shows that for weakly interacting mixtures - that is, where the differences in the interatomic potentials are small - the structure factors in that range $0 \leq q \leq q_o$ can be significantly different from those calculated from the hard sphere model, the difference being dependent on the relative strengths (magnitude and sign of $\mathcal{R}$ and γ) of the potentials. Although a comparison with experiment of the structure factors for arbitrary q is at present not possible because of lack of experimental scattering data, the conclusion arrived at here are nonetheless of considerable interest.

For example, in the theory of Faber and Ziman (1965) of the electrical resistivity of mixtures of simple metals, one has essentially to integrate the scattering function I(q), Eqn. (2.27), with a weighting

factor q^3, from $q = 0$ to $2q_F$, where q_F is the Fermi wave number of the electrons. The calculations have hitherto been performed either using the substitutional hypothesis or the hard sphere structure factors with different σ. For multi-valent metals, $2q_F > q_o$ so that the integration extends beyond the first peak and hence the use of hard sphere structure factors would form a good approximation. However, for monovalent metals $2q_F < q_o$, so that the modifications of the hard sphere structure factors at low q would, in general, have to be taken into account to obtain fully quantitative results. Since the interatomic potentials in metal alloys are not so well known, a useful procedure might be to choose a simple analytic form for $\chi_{ij}(r)$ and fix the parameters such that the long wavelength limit of all three structure factors agrees with those derived from thermodynamic data. The band structure and Madelung energy also depend on the structure factors and a similar procedure might be advantageous there too.

Finally we recall from Chapters 4 and 5 that the long wavelength limit of S_{CC} and other structure factors for compound-forming molten systems vary with concentration in a spectacularly different manner than for the conformal or weakly interacting mixtures. In these (compound-forming) systems the associative tendency

(characterised by stoichiometry) between the atoms is very strong and the method of calculating $S_{CC}(q)$, etc. presented here is not sufficient. Recently Ruppersberg and Eggar (1975) have measured from neutron scattering $S_{CC}(q)$ for LiPb mixture at the compound forming concentration Li_4Pb, and $S_{CC}(q)$ shows oscillations which are of much larger amplitude and which damp less rapidly than $S_{CC}(q)$ of Fig. 6.6. It was shown in Chapters 4 and 5, that the concentration fluctuations $S_{CC}(0)$ and other thermodynamic properties of the compound forming molten systems may be quantitatively explained on the basis of formation of appropriate chemical complexes. Recent work [Bhatia and Ratti, to be published] indicates that the idea of complex formation can also satisfactorily explain the neutron scattering data.

BIBLIOGRAPHY

Abowitz, G. and Gordon, R.B. (1962), J. Chem. Phys. 37, 125.

Ashcroft, N.W. and Langreth, D.C. (1967), Phys. Rev. 155, 682.

Ashcroft, N.W. and Lekner, J. (1966), Phys. Rev. 145, 83.

Barfield, R.N. and Schneider, W.G. (1959), J. Chem. Phys. 31, 488.

Bent, H.E. and Hilderbrand, J.H. (1927), J. Am. Chem. Soc. 49, 3011.

Bhatia, A.B. and Hargrove, W.H. (1973), Lett. Nuovo Cimento 8, 1025.

Bhatia, A.B. and Hargrove, W.H. (1974), Phys. Rev. B 10, 3186.

Bhatia, A.B., Hargrove, W.H. and March, N.H. (1973), J. Phys. C 6, 621.

Bhatia, A.B., Hargrove, W.H. and Thornton, D.E. (1974), Phys. Rev. B 9, 435.

Bhatia, A.B. and March, N.H. (1975), J. Phys. F 5, 1100 and private communication.

Bhatia, A.B. and Thornton, D.E. (1970), Phys. Rev. B 2, 3004.

Bhatia, A.B. and Thornton, D.E. (1971), Phys. Rev. B 4, 2325.

Brout, R.H. (1965), Phase Transitions, Benjamin, New York.

Cole, G.H.A. (1967), The Statistical Theory of Classical Simple Dense Fluids, Pergamon Press.

Croxton, C.A. (1974), Liquid State Physics - A Statistical Mechanical Introduction, Cambridge University Press, London.

Cutler, M. (1971), Phil. Mag. 24, 381.

Darken, L.S. (1967), Trans. Metall. Soc. AIME (Am. Inst. Min. Metall. Pet. Eng.) 239, 80.

Degenkolbe, J. and Sauerwald, F. (1952), Z. Anorg. Chem. 271, 324.

Egelstaff, P.A., Page, D.I. and Powles, J.G. (1971), Molec. Phys. 20, 881.

Enderby, J.E. and Collings, E.W. (1970), J. Non-crystal. Sol. 4, 161.

Enderby, J.E. and North, D.M. (1968), Phys. Chem. Liq. 1, 1.

Enderby, J.E., North, D.M. and Egelstaff, P.A. (1966), Phil. Mag. 14, 961.

Enderby, J.E. and Simmons, C.J. (1969), Phil. Mag. 20, 125.

Faber, T.E. (1972), Introduction to the Theory of Liquid Metals, Cambridge University Press, London.

Faber, T.E. and Ziman, J. M. (1965), Phil. Mag. 11, 153.

Flory, P.J. (1942), J. Chem. Phys. 10, 51.

Flory, P.J. (1953), Principles of Polymer Chemistry, Cornell University Press, Ithaca, N.Y.

Gubbins, K.E., Gray, C.G., Egelstaff, P.A. and Anath, M.S. (1973), Molec. Phys. 25, 1353.

Guggenheim, A.E. (1952), Mixtures, Oxford University Press, London.

Hager, J.P., Howard, S.M. and Jones, J.H. (1970), Metall. Transactions 1, 415.

Hultgren, R.R., Orr, R.L., Anderson, P.D. and Kelly, K.K. (1963), Selected Values of Thermodynamic Properties of Metals and Alloys, Wiley, New York.

Ichikawa, K. and Thompson, J.C. (1973), J. Chem. Phys. 59, 1680.

Krishnan, K.S. and Bhatia, A.B. (1944), Proc. Nat. Acad. Sci. India 14, 153.

Lebowitz, J.L. (1964), Phys. Rev. 133, A895.

Longuet-Higgins, H.C. (1951), Proc. Roy. Soc. (London) A205, 247.

March, N.H., Tosi, M.P. and Bhatia, A.B. (1973), J. Phys. C 6, L59.

McAlister, S.P. and Turner, R. (1972), J. Phys. F 2, L51.

McAlister, S.P. and Crozier, E.D. (1974), J. Phys. C 7, 3509.

McAlister, S.P., Crozier, E.D. and Cochran, J.F. (1973), J. Phys. C 6, 2269.

Nakamura, Y. and Shimoji, M. (1971),Trans. Farad. Soc. 67, 1270.

Page, D.I. and Mika, K. (1971), J. Phys. C 4, 3034.

Percus, J.K. (1962), Phys. Rev. Letters 8, 462.

Percus, J.K. and Yevick, G.J. (1958), Phys. Rev. 110, 1.

Progogine, I. (1957), The Molecular Theory of Solutions, North-Holland, New York.

Rowlinson, J.S. (1969), Liquids and Liquid Mixtures, second ed., Butterworth, London.

Ruppersberg, H. and Egger, H. (1975), J. Chem. Phys. 63, 4095.

Takeuchi, S., Uemura, O. and Ikeda, S. (1973), The Properties of Liquid Metals, Proc. Second Int. Conf. Ed. S. Takeuchi, Taylor and Francis Ltd., London.

Thiele, E. (1963), J. Chem. Phys. 39, 474.

Thompson, J.C. (1974), J. de Phys. (Colloque C4) 35, 367.

Turner, R. (1973), J. Phys. F 3, L57.

Vanstone, E. (1911), Trans. Faraday Soc. 7, 42.

Wertheim, M.S. (1963), Phys. Rev. Letters 10, 321.

Wilder, J.C. and Elliot, J. (1960), J. Electrochem. Soc. 107, 628.

Woodhead-Galloway, J. and Gaskell, T. (1968), J. Phys. C 1, 1472.

Woodhead-Galloway, J., Gaskell, T. and March, N.H. (1968), J. Phys. C 1, 271.

APPENDIX 1

The formulation of Chapter 4 does not work with G', introduced in Chapter 5, but rather with the derived quantities γ_i which are related to G' by

$$RT \ln \gamma_i = (\partial G/\partial n_i)_{T,P,n'} - G_i^{(o)} - RT \ln(n_i/n)$$

$$= (\partial G'/\partial n_i)_{T,P,n'} - RT \ln(n_i/n) \ . \qquad (A.1)$$

$\ln \gamma_i$ are zero if the ternary solution of A, B and $A_\mu B_\nu$ is ideal. In (A.1) the suffix n' means that in differentiating with respect to n_i, all other n_j are kept constant. Because of the extensive property of G', $(\partial G'/\partial n_i)$ and hence $\ln \gamma_i$ satisfy Gibbs-Duhem type of relations

$$\sum_i n_i (\ln \partial \gamma_i/\partial n_j)_{T,P,n'} = 0 \ . \qquad (A.2)$$

Since $G' = \sum_i n_i (\partial G'/\partial n_i)_{T,P,n'}$, one has from (5.2)

$$G_M = -n_3 g + RT \sum_i n_i \ln(n_i/n) + RT \sum_i n_i \ln \gamma_i \qquad (A.3)$$

and the equilibrium condition (5.5) gives

$$(n_1\gamma_1/n)^\mu (n_2\gamma_2/n)^\nu = (n_3\gamma_3/n)\exp[-g/RT] \ , \qquad (A.4)$$

(A.3) and (A.4) are the same as given in Chapter 4. The advantage of using γ_i is that like (A.4), some

of the formulas can be derived with a minimum of algebra and expressed compactly. For example, the activity a_A is simply $(\gamma_1 n_1/n)$. However, since in theoretical work it is the G' which is first calculated and γ_i are the derived quantities, we have not used here the formulation of Chapter 4. The two treatments are, of course, equivalent.

For the approximation (a) for G', expression (5.7), γ_i's are given by Eqn. (4.11), i.e.

$$RT \ln \gamma_i = \sum_{r=1}^{3} \omega_{ir}(n_r/n)\omega_{ir} - \sum_{r<s}\sum (n_r/n)(n_s/n)\omega_{rs} \quad . \qquad (A.5)$$

For approximation (b)

$$RT \ln \gamma_1 = RT[1 + \ln \frac{n}{\mathcal{N}} - \frac{n}{\mathcal{N}}] + \frac{1}{\mathcal{N}}(n_3 v_{13} + n_2 v_{12}) - \frac{1}{\mathcal{N}^2}\sum_{i<j}\sum n_i n_j v_{ij}$$

$$RT \ln \gamma_2 = RT[1 + \ln \frac{n}{\mathcal{N}} - \frac{n}{\mathcal{N}}] + \frac{1}{\mathcal{N}}(n_1 v_{12} + n_3 v_{23}) - \frac{1}{\mathcal{N}^2}\sum_{i<j}\sum n_i n_j v_{ij}$$

$$RT \ln \gamma_3 = RT[1 + \ln \frac{n(\mu+\nu)}{\mathcal{N}} - \frac{n(\mu+\nu)}{\mathcal{N}}] + \frac{1}{\mathcal{N}}(n_1 v_{13} + n_2 v_{23})$$

$$- \frac{\mu+\nu}{\mathcal{N}^2}\sum_{i<j}\sum n_i n_j v_i v_j \quad . \qquad (A.6)$$